THE DURABILITY OF ADHESION OF POLYSULFIDE SEALANTS TO GLASS

A dissertation presented in part fulfilment of requirements for the degree of

DOCTOR OF PHILOSOPHY

by

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DECLARATION

All the work included in this dissertation is that of the author, unless otherwise stated.

Unless otherwise stated the work was carried out at MORTON INTERNATIONAL Ltd. with some specialist work at DE MONTFORT UNIVERSITY and LOUGHBOROUGH UNIVERSITY.

None has been used for any other degree or qualification.

Signed

G.B.Lowe

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TRAINING

The following courses ,seminars and meetings were attended in furthering the authors understanding of adhesion and associated problems.

Adhesion Conference City University March 1988

Adhesion for Automotive Construction PRI Symposium Oct. 1988

Use of Dynamic Mechanical Thermal Analysis equipment - Private One Day Intensive Course by POLYMER LABORATORIES Ltd. Feb 1989

One Day symposium Adhesion and Surface Analysis University of Technology Loughborough Dec 1988

Day discussion with Dr M Gick on Performance of Polysulfides in water (ref 36) Aug 1988

Discussions with I.C.I.Ltd on fillers (see 2.3.2) June 1988

Discussions with E.C.C.Ltd on fillers (see 2.3.2) July 1988

Discussions with Monsanto on plasticisers (see 2.3.4) March 1989

Discussion with Exxon on plasticisers March 1989

Surface treatment and Analysis for Adhesive bonding - PRI Symposium Feb 1989

One day course on Surface Analysis UMIST 1989

Discussions with York University Oxidation group Feb 1989

Adhesion symposium P.R.I. december 1991

Collaboration with Oxford Polytechnic on Link programme

Adhesion Conference City University March 1992

Structural Adhesives in Engineering 111 Bristol University June 1992

Analysis and experimental group Oxford polytechnic Link project

CONTENTS

1 ABSTRACT

A number of polysulfide based sealants similar to those used commercially in insulated glass manufacture were prepared and used in this programme of work.

The formulations were designed to cover the spectrum of formulations sold commercially, especially with respect to polymer content, and to this end a number of commercial sealants were tested in order to ensure comparability.

The sealants were tested in glass/ sealant/ glass joints and examined for changes in joint strength and adhesion properties. Films of the sealant were subjected to the same ageing conditions and their physical properties checked.

The rate of change of adhesion properties was compared with the diffusion of water vapour into the cured films as measured by mass uptake experiments. The mode of failure was noted.

The changes were also examined chemically by surface analysis and the results examined for a relationship between formulation changes , such as polymer content , with diffusion rate which in turn could be related to onset of adhesion bond loss.

The results show that the primary cause of adhesion failure is plasticiser migration to the interface causing weakening of the interface and eventual adhesion failure. The diffusion of water into the sealant mass in the joints plasticises the sealant causing a lowering of the modulus of the sealant and creating the thermodynamic conditions to cause plasticiser migration.

2. INTRODUCTION

2.1 INSULATED GLASS

Insulated glass currently consumes a large amount of glass and sealant. The growth of the industry can be demonstrated by the statistical market size data found in the literature (1&2) and reproduced in reduced form here (Tables 1a & b). These tables show the increase of the usage of insulated glass in the U.K. from 6.5 to 15×10^6 m^2 between 1983 and 1987 and 17 $\times 10^6$ m^2 in 1988. The tables also show the types of sealants used and their respective market share. For completion the tables also show comparative data for North America.

In the U.K the tables show a period of sustained growth between 1983 to 1988 of over 250%.

The tables show that the predominant sealant in each European country is based on polysulfide technology. The total European market uses almost 10,000 tonnes of polysulfide polymer per annum, and whilst the sealant only represents 4% of the finished product cost it represents a major element in the integrity of the unit with respect to

TABLE 1a COMMERCIAL DATA SHOWING THE GROWTH OF THE INSULATING GLASS MARKET 1983 TO 1987

1983 – IG MARKET, square area and percentage sealant type

	Metres² Millions	*Polysulphide %*	*Polyurethane %*	*Hot Melt Butyl %*	*Silicone %*
W. GERMANY	17	83	15	2	—
FRANCE	9	84	8	4	4
ITALY	6	79	2	3	16
SWEDEN	2	88	12	—	—
SWITZERLAND	1.5	57	7	—	36
NORWAY	1.5	64	36	—	—
DENMARK	2	79	21	—	—
FINLAND	1	72	14	—	14
BELGIUM/HOLLAND	6	96	3	1	—
AUSTRIA	1.5	92	7	1	—
U.K.	6.5	76	12	7	5
	54.0	82	11	2	4
NORTH AMERICA	37	60	15	20	5
Metres² Millions =	91.0	66.56	11.46	8.80	4.18
Market Share % =		73%	12%	10%	5%

1987 – IG MARKET

Population Millions	*Country*	*Metres² Millions*	*Polysulphide %*	*Polyurethane %*	*Hot Melt %*	*Silicone %*	*Other %*
62	*W. GERMANY*	18.0	83	15	2	—	
55	*FRANCE*	7.1	68	14	10	8	
57	*ITALY*	5.2	79	2	3	16	
8	*SWEDEN*	1.7	90	10	—	—	
7	*SWITZERLAND*	1.4	57	7	—	36	
4	*NORWAY*	2.2	90	10	—	—	
5	*DENMARK*	1.9	95	5	—	—	
5	*FINLAND*	0.8	72	14	—	14	
24	*BELGIUM/ HOLLAND*	5.0	96	3	1	—	
8	*AUSTRIA*	2.0	92	7	1	—	
56	*U.K.*	15.0	64	12	12	7	5
291		60.30	78	11	5	5	1
234	*U.S.A.*	48.50	53	14	28	5	—
Metres² Millions		108.80	72.51	13.38	16.68	5.49	0.74
Market Share %			67	12	15	5	1

FIGURES are based on independent surveys undertaken by Thiokol Chemicals in co-operation with leading U.S.A. and European IG manufacturers.

TABLE 1b 1988 MARKET STATISTICS

1988 – IG MARKET

	Sq Mtrs (Millions)	LP %	PU %	HMB %	Silicone %	Other %
W GERMANY	22.0	83	14	2	1	
FRANCE	8.0	67	14	10	9	
ITALY	8.5	78	3	3	16	
SWEDEN	2.3	90	10	–	–	
SWITZERLAND	2.0	58	7	–	35	
NORWAY	1.7	90	10	–	–	
DENMARK	2.0	95	5	–	–	
FINLAND	1.0	70	14		16	
BELGIUM/HOLLAND	4.5	95	3	2		
AUSTRIA	2.0	92	7	1		
U.K.	17.0	60	12	12	9	7
	71.0	76	11	5	7	1

LP = POLYSULFIDE BASED SEALANTS

PU = POLYURETHANE BASED SEALANTS

HMB = HOT MELT BUTYL SEALANTS

holding the unit together, and should adhesion loss occur the repair costs could be substantial. Insulated glass units which have been properly constructed and glazed have an anticipated functional life well in excess of ten years. Unfortunately this is not always met, and some units fail in under five years.

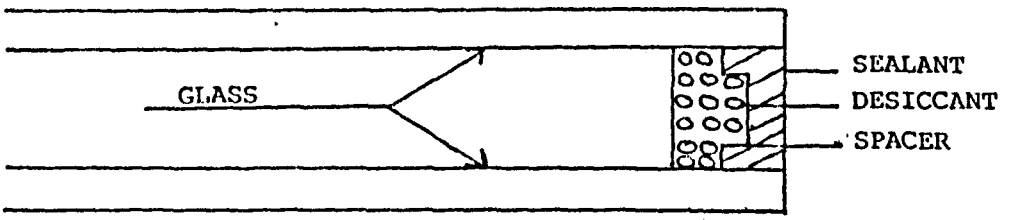
A typical insulated glass unit consists of two panes of 4mm. thick glass separated by a hollow spacer tube. The tube is generally extruded or rolled aluminium and is filled with a desiccant, which is either silica-gel or molecular sieve. The whole unit is held together with a perimeter sealant, known as the insulated glass sealant.

A typical construction of an insulated glass unit is shown in figure 1. Plate 1 which shows the relationship between the insulated glass unit and the glazing frame. Plate 2 shows a failed unit, in this case failure occurred after three years. In the upper part of the plate the pointer indicates an area of adhesion failure, the lower part shows the extensive water ingress due to failure. This particular unit failed by adhesion loss between glass and sealant after it had stood in water contained in the frame rebate.

It is because of these early failures that this work was undertaken with the objective of studying the role of atmospheric moisture on the adhesive bond.

FIGURE 1 Typical construction of the edge of an insulated glass unit

FIGURE 1 Typical construction of the edge of an insulated glass unit



VIEW OF SPACER INSIDE UNIT
SHOWING SLOTS FOR PASSAGE OF MOISTURE

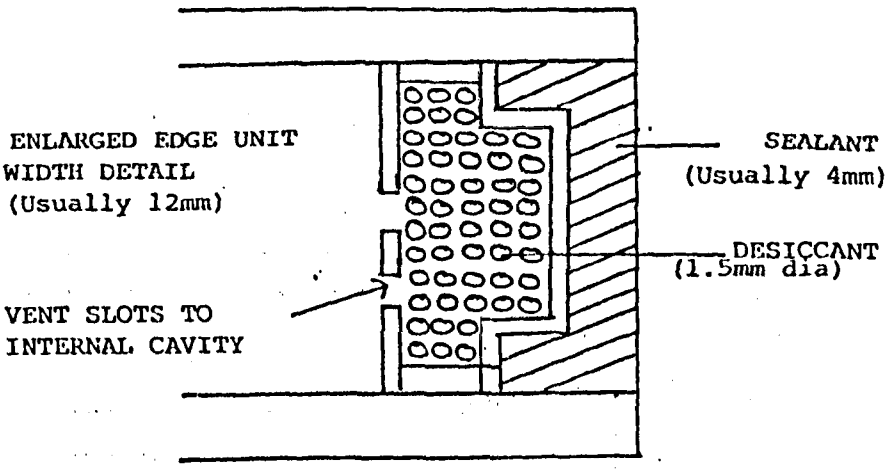


PLATE 1 SHOWING A TYPICAL EXAMPLE OF INSULATED GLASS UNITS

a shows the unglazed unit

b shows the glazed unit in cut-away form. The cavity below the unit is where water can collect thus creating the situation for long term immersion or high humidity.

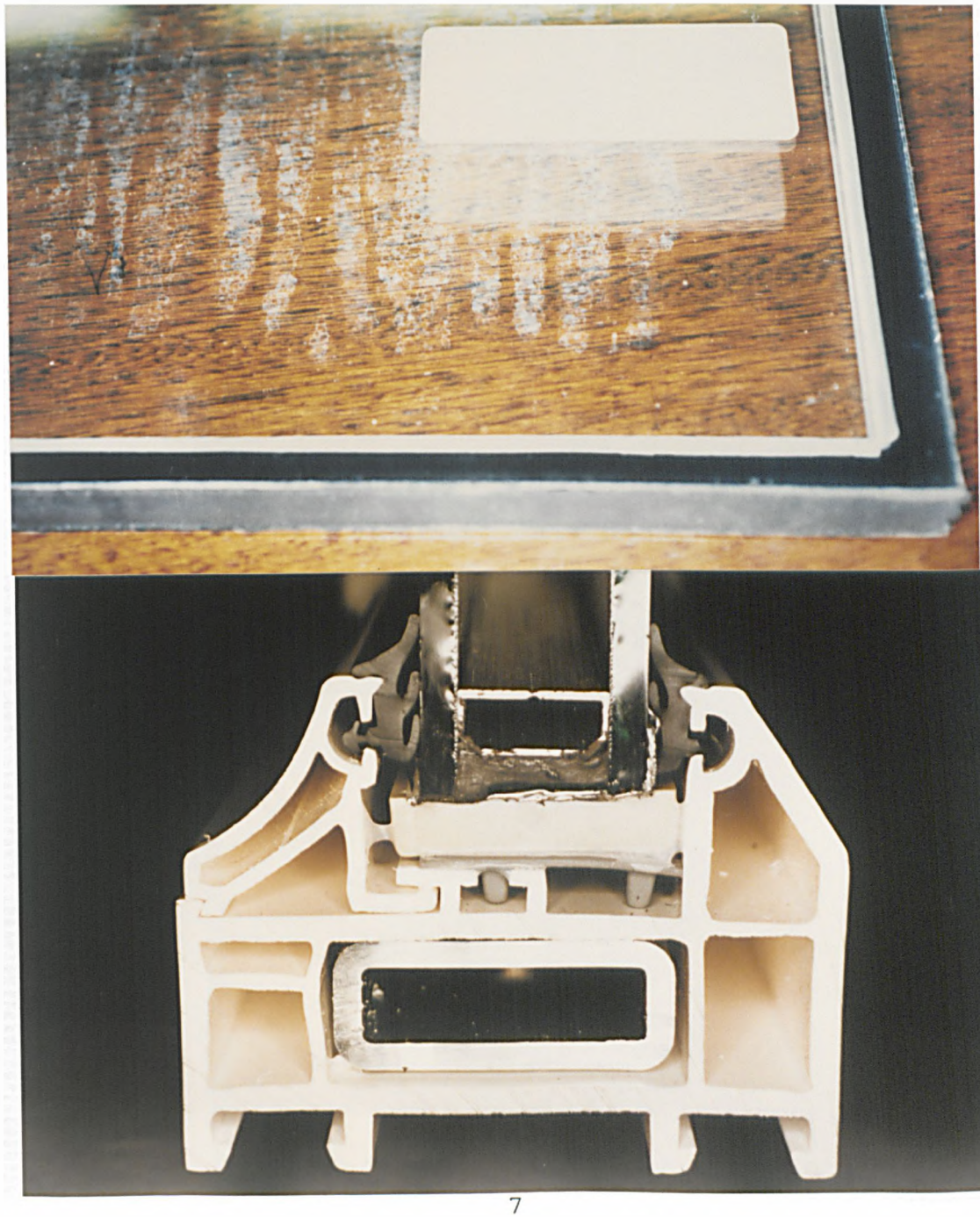
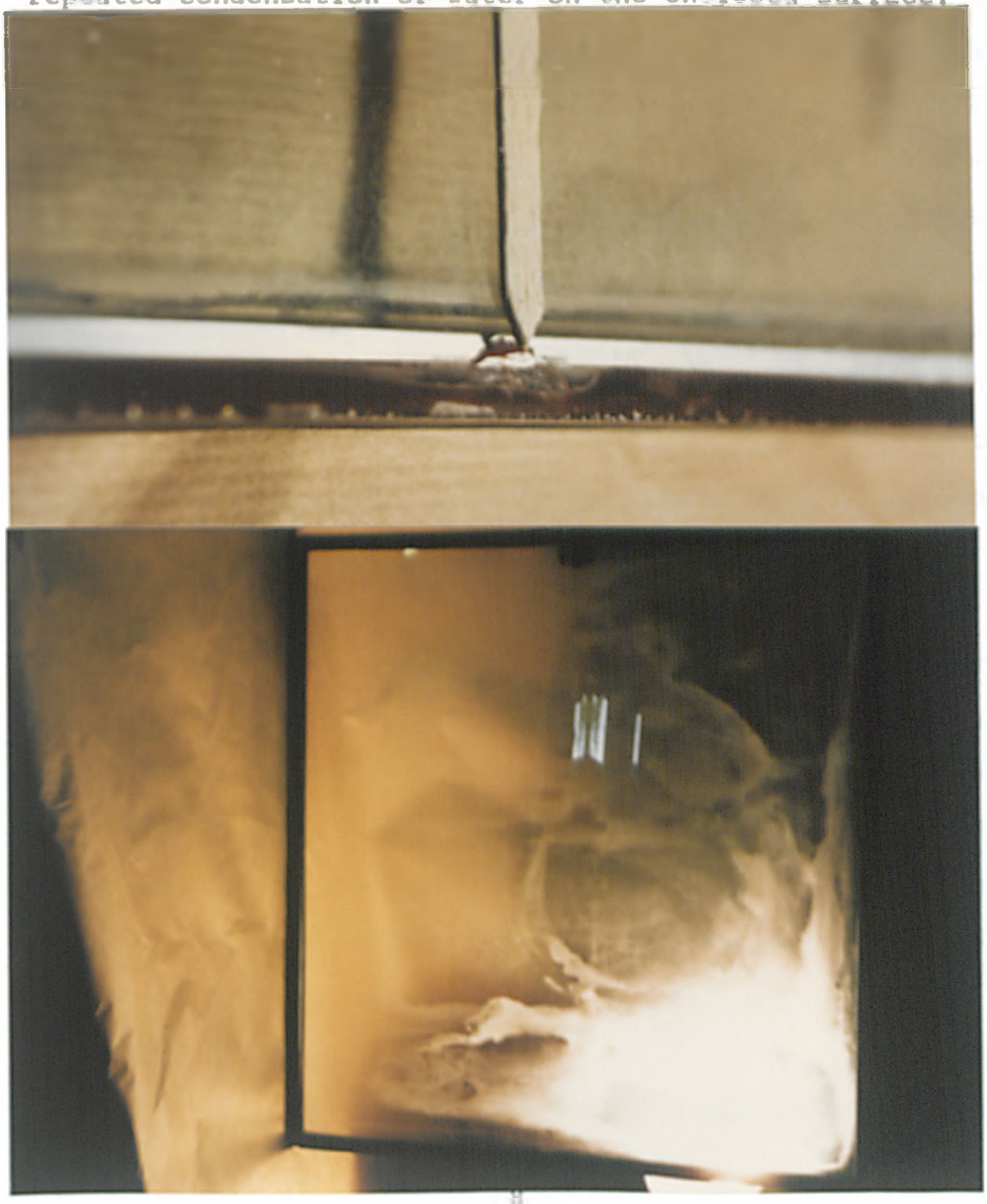


PLATE 2 SHOWING A TYPICAL FAILURE OF A UNIT AFTER WATER ATTACK.

The upper plate shows the point of adhesion loss

The lower plate shows an inorganic deposit formed by repeated condensation of water on the enclosed surface.



2.2 REVIEW OF EARLY WORK ON FAILURE OF UNITS

Premature failure occurs in units due to a number of mechanisms, but is first observed as misting between the panes of glass due to moisture ingress. Whilst the desiccant contained in the unit will absorb some of the moisture during the initial stages it will eventually become saturated when misting occurs. There is no known evidence to suggest that any of the commonly used sealants show any major variation in their moisture vapour transmission rates on ageing, and therefore the majority of failures are reported as adhesion loss between the sealant and the glass. The performance of insulating glass units is tested using the same technique regardless of sealant type, one such test procedure is given in reference (3).

Durability of insulated glass units have been a concern of the industry for many years. As early as 1970 the National Bureau of Standards of America called a conference entitled Durability of Insulated Glass, which brought together American experts to debate the problem. The proceedings were published as Building Science Series 20 by the U.S. Department of Commerce.

Much of the early work was directed at observing the

behaviour of insulated glass units when subjected to standard test procedures. Some of the work was aimed at producing test methods and domestic specifications by which the insulated glass units could be judged.

Some of the findings of these earlier workers are reported by K.R. Solvason and A.G. Wilson (4), and R.J. Mazzoni and L.J. King (5). These papers concentrate on the relationship between moisture vapour transmission rate (MVTR) and service life. Solvason (6) recognised the stresses imposed on the edges of the insulated glass unit, and the effects on the useful life of the unit assembly.

The relationship between MVTRs and service life is further explored by Mazzoni in his article "Predicting the Service Life of Insulating Glass Units" (7).

It must be commented here that a change of terminology occurred around 1980 when the term DOUBLE GLAZING UNITS was replaced by the now more common INSULATED GLASS UNIT, which was used by Wicks in his article on "Design Aspects of Insulated Glass Units" (8).

The correlation between MVTR and service life is only valid in a few cases of well glazed insulated glass units. Many

of the premature failures cannot be explained so simplistically.

Some workers tried to explore the breakdown of insulating glass units by including a parameter relating to the glazing quality of those units. Such a worker, Backman, still resorted to MVTR as the main means for measuring failure (9), as did Quade (10) in his article on service life. The theme was continued by Brolin in his article "Penetration of Water Vapour into Insulated Glass Units" (11). Somewhat surprisingly Bachman later used diffusion and MVTR to try and predict the durability of insulated glass units (12 & 13).

Analysis of failures of construction sealants based on polysulfide polymers suggested the possibility of plasticiser migration as being a cause of failure (14), although this theory was not explored further during a prolonged study undertaken much later (15).

None of the earlier work gives a substantive solution to the cause of premature failures and it is the purpose of this thesis to evaluate one of the possible causes, namely water diffusion into the sealant and its effects on the glass-sealant interface.

2.3 AIM OF PROGRAMME

It was the aim of this work to examine the adhesion failure caused by high humidity and to study formulation variables that may have a bearing on the failure mode. In order to achieve this, it was planned to examine changes in the physical properties of sealants against time of exposure to high humidity. Simultaneously the mass uptake of water into the sealant was to be measured as well as the strengths and modes of failure of aged glass-sealant-glass adhesive joints.

3 SEALANTS

Morton International Ltd., are manufacturers of a range of sulfur based polymers supplied under the trade name of Thiokol Polysulfide polymers. The liquid forms of these polymers are referred to as LP polymers and are used extensively in the preparation of sealants and adhesives.

The sealant must perform a number of functions. These can be simply stated as a) having a low moisture vapour transmission rate to prevent moisture from the atmosphere entering the unit and condensing on the inner glass surface, b) having good adhesion to both glass and aluminium over the lifetime of the unit and c) having chemical resistance to any glazing compound, for example non-setting putties, paints etc., that may be used in the installation.

The sealants used in the construction of insulated glass units are generally two part, cold curing systems. The larger, polymer containing part, is referred to as the base, whilst the smaller portion is called the curative.

The compounds used in this work are polysulfides which are cured by oxidation. The oxidising agent is manganese dioxide and is contained in the curative.

Liquid Polysulfide polymers are usually prepared from bis(2- chloroethyl) formal and sodium polysulfide. The polymerisation is carried out in aqueous suspension and is a condensation reaction. Subsequent hydrolysis yields a very high (10^6) molecular weight product with -OH terminal groups. Reaction with NaSH and Na_2SO_3 produces a polymer with -SH terminal groups, the final molar mass being controlled by the level of NaSH used .

Liquid polysulfides are substantially straight chain thiol terminated polymers of diethyleneoxymethane with polysulfide linkages.

$$HS\text{-}(C_2H_4\text{-}O\text{-}CH_2\text{-}O\text{-}C_2H_4\text{-}S_x)_n\text{-}C_2H_4\text{-}O\text{-}CH_2\text{-}O\text{-}C_2H_4\text{-}SH$$

The value of x is found to be 2.4 on average

Addition of trichloropropane results in branching sites useful for crosslinking. The main polymers used in Insulating Glass Sealants are listed in table 2. The polymers are liquids at room temperature and cure to solid rubbers at ambient temperatures.

Brief technical reviews on the use of polysulfide liquid polymers in sealants is in "Sealants" edited by A. Damusis (17), "Adhesion and the Formulation of Adhesives" edited by W.C. Wake (18) and "Construction Sealants and

Adhesives" edited by Panek and Cook. (19).

TABLE 2 LIQUID POLYSULFIDE (LP) POLYMERS USED IN SEALANTS

The properties of the common polymers used in insulated glass sealant manufacture, data supplied by Morton International. The product LP2C, used in these experiments is described on page 17.

	LP33	LP3	LP977	LP32C
Number Average molar mass (Mn)	1000	1000	2600	4000
Number average degree of polymerisation	6	6	15	23
% trifunctional monomer (Mol %) (as trichloropropane)	0.5	2	2	0.5
Average thiol content (mol kg^{-1}) (as -SH value)	1.75	2.06	0.91	0.53
Average Viscosity at 25 ^{o} C (Pa.s)	1.75	1.15	12.5	46.5

Further information on the production of polysulfide rubbers is to be found in "Introduction to Rubber Technology" (16).

These together with "An Introduction to Cure Mechanism" by Ghatge et.al. (20) give a broad background to the subject.
A more detailed discussion on the preparation of the polysulfide LP polymers can be found in part three of "Polyethers" edited by Gaylord (21).

Further detail is available in "The Chemistry of Sulfides" edited by A.V. Tobolsky (22), who also deals with some of the reactions.

Whilst there is much documentation covering the use of liquid polysulfide polymers in sealants, little is known about the mechanism of failure, especially in insulated glass units.

3.1 BASE

The polysulfide known as LP2C and made by Morton International was chosen for these experiments, it has the following parameters :-

Number average molar mass (Mn).....4000

Number average degree of polymerisation....23

Trichloropropane addition (mol %) 2

Average thiol content (mol kg^{-1}).....0.60

Average viscosity at 25°C (Pa.s).....46

This polymer was chosen because it gives insulated glass sealants of the correct modulus and elasticity. It is also the most widely used polysulfide in this area.

Apart from the polymer, the base consists of fillers, plasticiser, pigment, thixotropic agent, and adhesion promoter. The formulator has a wide choice, and selection is often one of experience in using a particular product.

The base is filled to both control costs and rheological properties. The most common form of filler used is calcium carbonate. Calcium carbonate fillers are available in both precipitated and ground forms and due to the natural abundance of the parent material are relatively inexpensive.

The precipitated calcium carbonates have much smaller particle sizes than their ground counterparts. The precipitated version has 90% of particles below 1μm with its largest particle at 5μm., whilst the ground version has

a particle size distribution in the range 2 to 10 μm.

It has been found that the addition of a stearic acid coating to the carbonates help the fillers impart thixotropy and increased viscosity to the sealant compared to the non coated versions. It is also argued that the addition of the stearic acid coating gives increased polymer/filler adhesion and therefore leads to improved reinforcement.

In the case of the precipitated carbonates the stearic acid is added during the precipitation process, whereas with the ground product the stearic acid is added during the water slurry grinding process. Coating weights of between 0.5% and 3% of stearic acid are available for both forms of filler.

The larger particle size, ground, coated calcium carbonates are gaining some acceptance with formulators, whilst the precipitated carbonates have been used for a long time. It is acknowledged however that a system based entirely on precipitated calcium carbonate would not be practical due to excessive thickening. A mixture of both precipitated and ground carbonates was chosen for this work to give the desired balance of properties.

The precipitated product used was Winnofil SP, manufactured by I.C.I. Ltd.

Winnofil SP has a 3% stearic acid coating (23). The ground carbonate used was Polcarb S, which also has a stearic acid coating weight of 3%. Polcarb S is manufactured by E.C.C. Ltd., and is used within the sealant industry to assist in adding thixotropy to the system (24).

Whilst it is not necessary to pigment insulated glass sealants, it is often considered advisable to have a high degree of colour contrast between the polymer base compound and the curative. This allows the user a visual control to ensure complete mixing of base and curative as the reaction is heterogeneous and relies on the complete dispersion of the curing agent to cure properly. The pigment chosen was a rutile titanium dioxide manufactured by B.T.P. Ltd.

Plasticisers are used to aid addition of the fillers by lowering the viscosity of the polymer and to lower the modulus of the final compound. Plasticisers for polysulfide sealants generally belong to one of two groups. These two groups are the chlorinated paraffins and the phthalate esters. The chlorinated paraffins have become less popular due to their poor viscosity/temperature relationship in that their solidification point can be as high as 5°C and this makes the sealant difficult to mix at lower temperatures.

The choice of plasticiser is dependent on its compatibility with the polymer, the viscosity of the resultant blend and the volatility of the plasticiser at moderate temperatures (50-70 ^{0}C). In this work the product Santiciser 278 produced by Monsanto Ltd was chosen (25). It is described as being texanol benzyl phthalate and has the following characteristics:

CH_3-CH-CH(OH)-C(CH_3)$_2$-CH_2-O-C-Ph-C-O-CH_2-Ph

CH_3 O O

molar mass	485
specific gravity (g.cm^{-3})	1.093 - 1.101
surface tension	34.8 mNm^{-1}
solubility in water	practically zero

It is not possible to rely on the fillers alone to obtain the correct combination of rheological properties; a thixotrope is also added. For these experiments Bentone SD-2, manufactured by Bakers Castor Oil Company was chosen. This is a blend of bentonite clay and sulfonated castor oil and is supplied in powder form. When the powder is added to the plasticiser it swells forming a thixotropic paste. Normally only low concentrations of the thixotropic agent are required.

As cured polysulfide rubbers do not have a high level of inherent adhesion

to glass, it is necessary to add an adhesion promoter. The most common types of promoter used in sealant technology are the silanes.

The use and function of silane adhesion promoters or coupling agents are described by Comyn (26 & 27). Further studies on the use of silane adhesion promoters can be found in the Degussa bulletins which deal with the uses of 3-glycidoxypropyl- trimethoxy silane, including their use in coatings (28,29 & 30).

The silane adhesion promoter chosen for these experiments was Silane A187 from Union Carbide, which is 3-glycidoxypropyl-trimethoxysilane (31), which is described in their application notes (32 & 33).

3.2 CURATIVE

Polysulfide liquids are cured by organic or inorganic oxidising agents. The most usual curing agents used in sealant technology are the dioxides of manganese and lead, and to a lesser extent the peroxides of calcium and zinc.

For insulated glass sealants the most common curing agent is manganese dioxide. The product is not pure MnO_2, but is activated by addition of alkali metal salts or hydroxides. The outline of the production of the oxide is covered in the "Chemistry of the Elements" (34). A detailed study into the use and reactions of manganese dioxide was given by Fatiadi in "Synthesis" (35). The variations in cure characteristics due to different manganese dioxides was studied by Cox (36) in an effort to characterise the differences found between manufacturers.

The product chosen was the manganese dioxide FA grade produced by Riedel de Haen. It is activated by sodium hydroxide during a digestion process, described in the patent owned by the manufacturer, (USP 4104189).

The reaction between polysulfides and manganese dioxide proceeds relatively slowly, especially when the reactants are diluted with fillers and plasticisers. It is therefore necessary to use catalysts to accelerate the cure to an acceptable level. Although the choice of catalyst is wide, the product tetramethylthiuram disulphide (TMTD) was selected as being the most appropriate.

The curative is a paste formed by dispersing manganese dioxide and catalyst in a plasticiser, usually the same type of plasticiser as used in the base, to ensure compatibility.

4 THEORY OF CURE MECHANISM

Early reference to the use of manganese dioxide as a curing agent was referred to in articles concerning paint driers (37) and (38).

Unfortunately earlier workers concentrated on the more practical aspects of the cure as typified by Hanhela, Huang, Paul and Symes (39). However the radical mechanism had been proposed by Tobolsky (22) as well as Berenbaum and other workers associated with Thiokol Chemicals (now known as Morton International) who are the manufacturers of the polysulfide LP polymers.

The variations in cure due to variations in manganese dioxide were explored by Minkin (40) whilst oxidative cure using non-metallic organic oxidising agents was studied by Khan(41).

The cure of polysulfides is believed to proceed via a free radical mechanism. Studies by Capozzi and Modena (42) on aliphatic and aromatic thiols used simple model compounds. Their mechanism requires the formation of an oxygen atom and the subsequent cure proceeds by the following steps:

$$MO_2 \rightarrow MO + O^{\cdot}$$

(M = metal)

$$2\ HS\text{-}R\text{-}SH + O^{\cdot} \rightarrow 2\ HS\text{-}R\text{-}S^{\cdot} + H_2O$$

$$2\ HS\text{-}R\text{-}S^{\cdot} \rightarrow HS\text{-}R\text{-}S\text{-}S\text{-}R\text{-}SH$$

There is also the possibility of forming a transient radical complex

$$HS\text{-}R\text{-}S\text{-}S\text{-}SHOM^{\cdot}$$

There are a number of problems with this simple mechanism, one is that the reaction is known to be catalysed by an increase in alkali content and proceeds either very slowly or not at all if water is excluded before the reaction begins.

Later workers have attempted to elucidate the apparently complex reaction mechanism by the use of nuclear magnetic resonance (NMR). Minkin et.al. (43, 44 & 45) suggested the possibility of intermediate complexes with the oxygen donor.

Work in examining the role of curing agents with polysulfides (46) attempted to quantify the level of curing agent to give the best cure. However no worker has successfully explained the differences in mechanical properties

of the cured polymers when cured by different metal peroxides.

With manganese dioxide curing agents the situation is further complicated by the fact that manufacturers do not reveal the details of the degree of alkalination carried out in producing the end product. Also the alkali present can be taken from any of the hydroxides that are soluble in water. In practice sodium or potassium hydroxide are most commonly selected.

Further studies are currently being investigated by Gilbert and Coates at York University (47), who has demonstrated the presence of free radicals in the polysulfide polymer. This work is a detailed study into the oxidative cure reaction between manganese dioxide and polysulfide.

5 EXPERIMENTAL CONDITIONS

5.1 PREPARATION OF SEALANT FORMULATIONS

5.1.1 BASE

In tables 3a and 3b all the formulations for the bases X1 to X10 used are given in parts by weight. Note should be made that the formulations are shown in an order that demonstrates the simple stepwise changes made to give property variations. Only the polymer and/or plasticiser content is varied in an attempt to give a spread of modulus properties without too many variations in formulation. The ingredients used are those described previously.

TABLE 3a FORMULATIONS OF BASE/ PARTS BY WEIGHT

(plasticiser content constant)

code No.	X1	X2	X7	X3	X8
polysulfide LP 2C	100	90	80	70	60
precipitated $CaCO_3$	25	25	25	25	25
phthalate ester	20	20	20	20	20
titanium dioxide	10	10	10	10	10
ground $CaCO_3$	25	25	25	25	25
bentonite	3	3	3	3	3
silane	3	3	3	3	3

TABLE 3b FORMULATION OF BASE/PARTS BY WEIGHT

(plasticiser content varied)

Code No.	X4	X9	X5	X10	X6
polysulfide LP 2C	50	80	70	60	50
precipitated $CaCO_3$	25	25	25	25	25
phthalate ester	20	40	50	60	70
titanium dioxide	10	10	10	10	10
ground $CaCO_3$	25	25	25	25	25
bentonite	3	3	3	3	3
silane	3	3	3	3	3

All the above compounds were made by first adding the calcium carbonate and titanium dioxide fillers to the liquid polymer and mixing in a high shear mixer to form a viscous paste. This takes 15 to 20 minutes. When the fillers were fully dispersed and no large particles remained the silane adhesion promoter and bentonite thixotrope were added. After mixing for fifteen minutes the resultant thick paste was reduced in viscosity by the addition of the phthalate ester plasticiser.

5.1.2 FORMULATION OF THE CURATIVE

The curative paste which is the same for all test systems has the following formulation, in parts by weight :-

manganese dioxide	10
phthalate ester	10
tetramethyl thiuram disulfide	0.5

The cure paste was made by dispersing the manganese dioxide and catalyst into the plasticiser by spatula, followed by two passes through a three-roll mill.

The mix ratio of each system was calculated on a weight to weight basis of

polysulfide : manganese dioxide = 10 : 1

5.2 AGEING CONDITIONS

The ageing conditions chosen of 60^{0}C and 95 - 100% relative humidity are similar to those used in standard insulating glass specifications (48). These particular ageing conditions were also chosen by Wegman et.al. and others to study the durability of adhesives (49 and 50).

The ageing conditions were generated in a stainless steel humidity cabinet manufactured by John Godrich Ltd. Unless otherwise stated all ageing tests were carried out in this cabinet.

5.3 SUMMARY OF CHOSEN EXPERIMENTAL TESTS

Using the formulations described above, glass - polysulfide - glass joints were prepared and, after curing, subjected to the specified ageing conditions. In this case however the strengths of the joints were measured at frequent intervals and the mode of failure examined.

The experiments were designed to evaluate the change in adhesion properties between the sealant and glass before ageing to changes in the sealants after ageing at elevated temperatures and high relative humidity for various periods of between 0 and 2 years.

The test methods to be used for evaluating the sealant properties were Dynamic Mechanical Thermal Analysis (DMTA), Differential Scanning Calorimetery (DSC), water uptake by sealants and cold water extraction. Tests associated with the adhesion work were surface analysis, polymer/plasticiser miscibility, adhesion build up on drying and the thermodynamic work of adhesion.

6. DYNAMIC MECHANICAL THERMAL ANALYSIS

Dynamic Mechanical Thermal Analysis (DMTA) measures the bulk rather than surface properties of polymer systems. However it can potentially be used to detect changes in the sealant due to ageing and water absorption.

It was hoped that the use of the DMTA would give some insight into the early changes of the sealant due to ageing.

6.1 THEORY OF D.M.T.A.

Dynamic mechanical thermal analysis (DMTA) of rubbers, plastics and composites over a wide range of temperatures and frequency provides detailed information about the chemical and physical structure of these materials and their performance characteristics. Variation of the dynamic storage modulus (E' or G') and the damping factor (Tan δ) with temperature and frequency allow characterisation of the viscoelastic properties of a particular material.

The basic principles of the DMTA technique are outlined below.

When a sinusoidal stress is applied to a perfectly elastic solid the

deformation (and hence the strain) occur exactly in phase with the applied stress. A completely viscous material will respond with the deformation lagging 90^0 behind the applied stress as shown in figure 2.

Stress is the force per unit area acting on a sample and is usually measured in Nm^{-2}, strain is the resultant deformation and is dimensionless. When a sinusoidal stress is applied to a visco-elastic material the behaviour is in-between that of a perfectly elastic and a perfectly viscous body and the resultant strain will lag behind the stress by an angle (δ) where $\delta < 90^0$. This is known as the loss angle. The magnitude of the loss angle δ is dependant upon the amount of internal motion occurring in the same frequency range as the imposed stress.

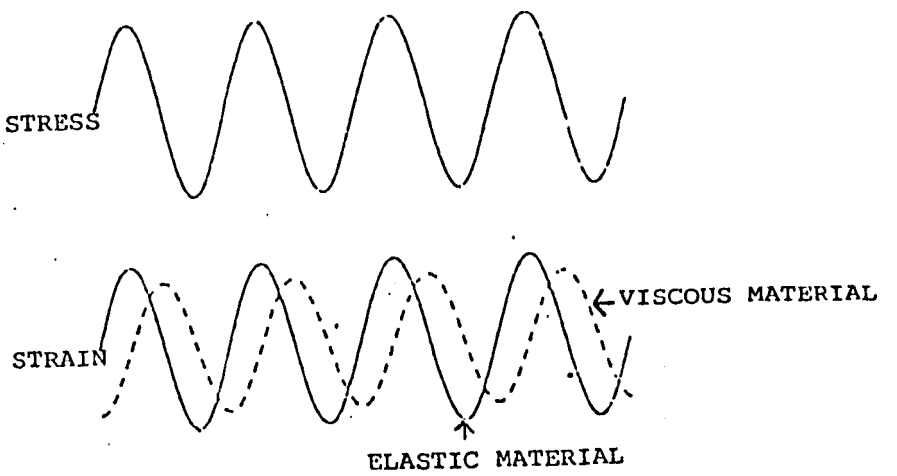


figure 2

The complex dynamic modulus (E* for bending or tensile measurements, G* for shear measurements) is defined as

for tensile $E^* = E' + iE''$

for shear $G^* = G' + iG''$

using the tensile argument only

E^* = stress amplitude / strain amplitude

The complex dynamic modulus, however, does not take into account the phase and it is therefore convenient to define the elastic and viscous components of the deformation as follows.

The storage modulus E' is defined as

$$E' = \frac{\text{amplitude of in phase stress component}}{\text{strain amplitude}}$$

and the loss modulus, E'' is defined as

$$E'' = \frac{\text{amplitude of out of phase stress component}}{\text{strain amplitude}}$$

The storage modulus is the elastic response and corresponds to completely

recoverable energy whereas the loss modulus is the viscous response corresponding to energy lost as heat.

The tangent of the loss angle, tan δ, is equal to the ratio of energy lost to energy stored per cycle.

$$\text{Tan } \delta = \frac{\text{loss modulus}}{\text{storage modulus}} = \frac{E''}{E'}$$

The DMTA technique detects all motional transitions and provides a sensitive means of studying the glass and other transitions in polymers.

DMTA measures the Modulus (E) and Loss Tangent (Tan δ) of a material as a function of temperature. The sample under evaluation is vibrated at a fixed frequency and amplitude and the forces measured using an appropriate transducer. The frequency and amplitude are chosen to suit the nature of the system being evaluated.

It should be noted that more than one frequency can be chosen for a particular experimental run, but multi-frequency runs do not always yield extra useful data.

6.2 EXPERIMENTAL CONDITIONS OF DMTA TEST

The DMTA experiments were measured on a DMTA Mark 2 manufactured by Polymer Laboratories Ltd. Samples were prepared by first casting a film 100mm x 100mm x 2mm of the test sealant onto a flat inert release surface and allowing it to cure for 7 days at 23°C and 50% relative humidity (RH). For details of the casting technique used see section 9 on water uptake.

After curing small samples measuring 10mm x 5mm x 2mm were taken from the film. The sample was mounted in the DMTA chamber using a single cantilever sample holder as shown in figure 3. The sample measurements were determined using a micrometer and are the average of three or more determinations.

It should be noted here that not all the formulated systems of tables 3a and 3b of section 5.1.1 were tested due to difficulty in preparing good films (X10 was omitted).

The conditions used were : start temperature -100°C, finish temperature + 100° C, heat rate 3° C/Min. and frequencies of 1 and 10 Hz.

The formulations were tested initially and then after the ageing periods of three months and one year under the prescribed test conditions of 60 °C and 95-100% R.H. A typical initial DMTA trace is shown in figure 4, and an

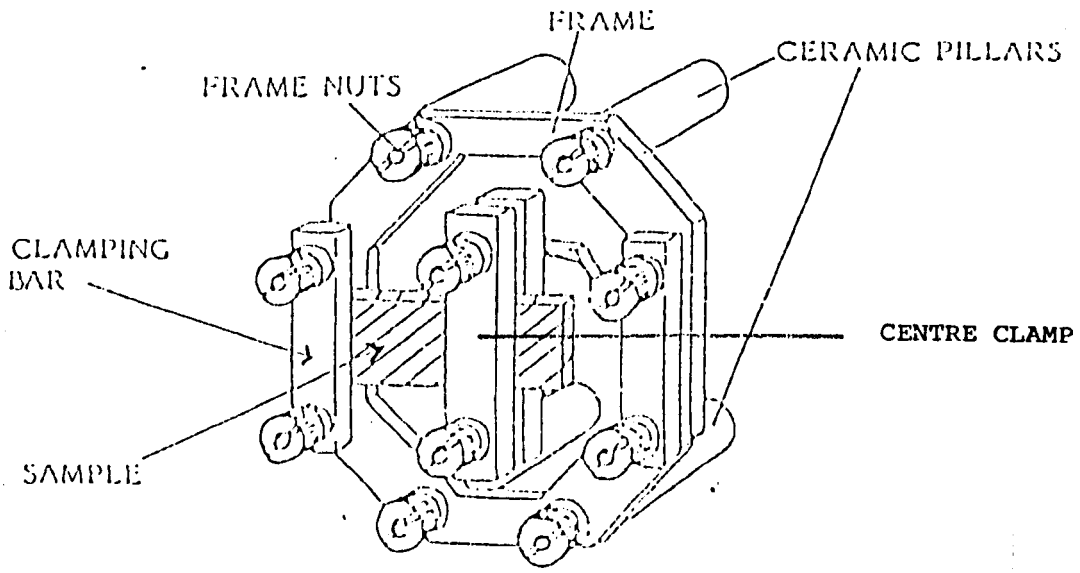
aged trace is shown in figure 5.

The aged samples were then dried to constant weight by heating in an oven at 45°C for 28 days and retested by DMTA. A typical trace of an aged and dried sample is shown in figure 6. Comparison of the three traces shows that there is little change in the modulus below the main transition, the extra transition in the aged sample as demonstrated in figure 5 was attributed to water which was not present initially or after drying.

Further examples of DMTA traces can be found in appendix A.

FIGURE 3 SAMPLE HOLDER FOR DMTA

showing the clamping arrangement for single cantilever mode



The sample is flexed by the centre clamp oscillating across the frame. The displacement is predetermined and the transducers measure the force required to affect the displacement.

FIGURE 4 DMTA TRACE OF FORMULATION X1 (UNAGED)

showing the modulus and Tan δ versus temperature

- - - - - 10 Hz . . ——— 1 Hz

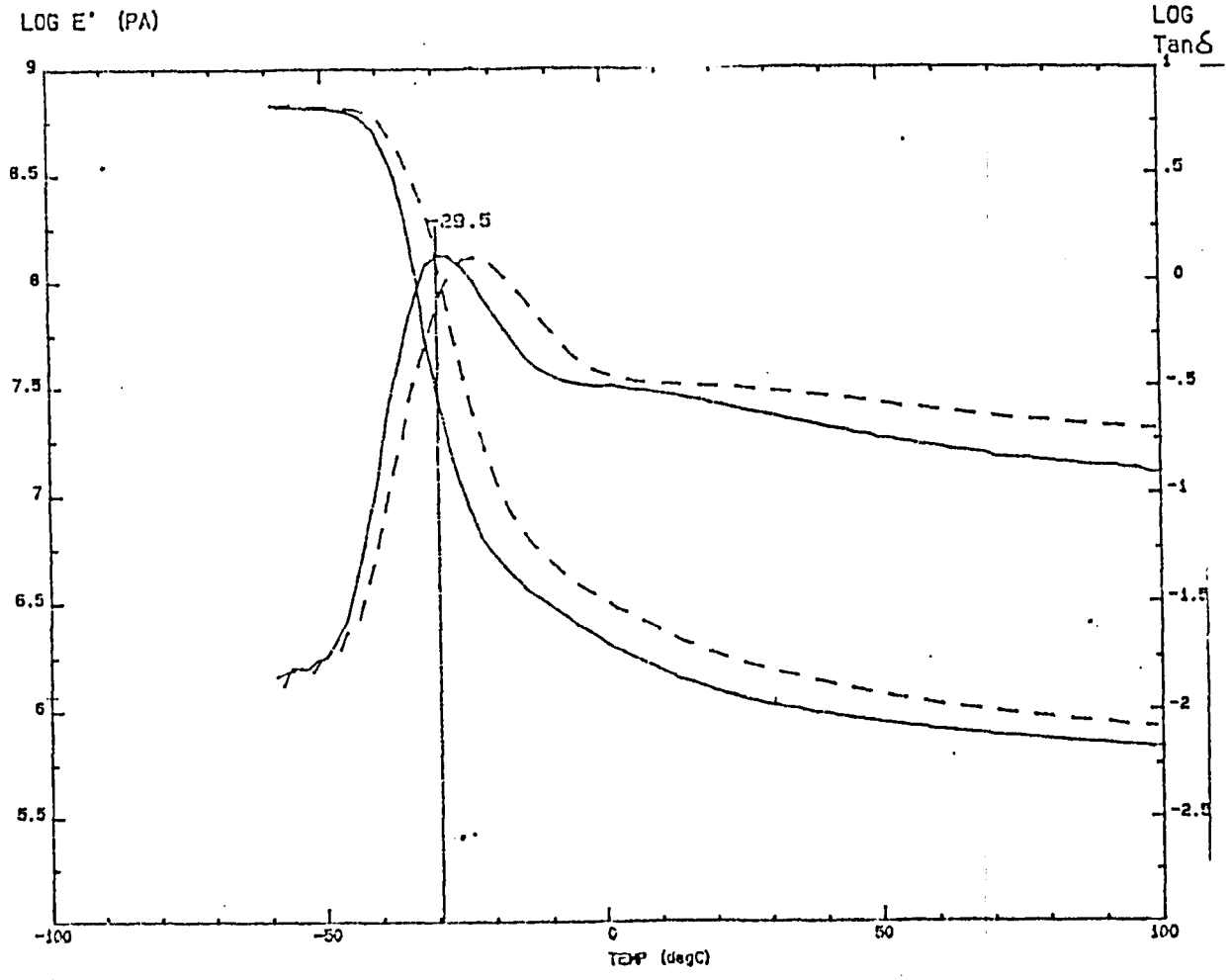


FIGURE 5 DMTA TRACE OF FORMULATION X1 AFTER HIGH HUMIDITY AGEING FOR A PERIOD OF 1 YEAR

measured immediately after removal from the test cabinet

note the extra transition at 5°C

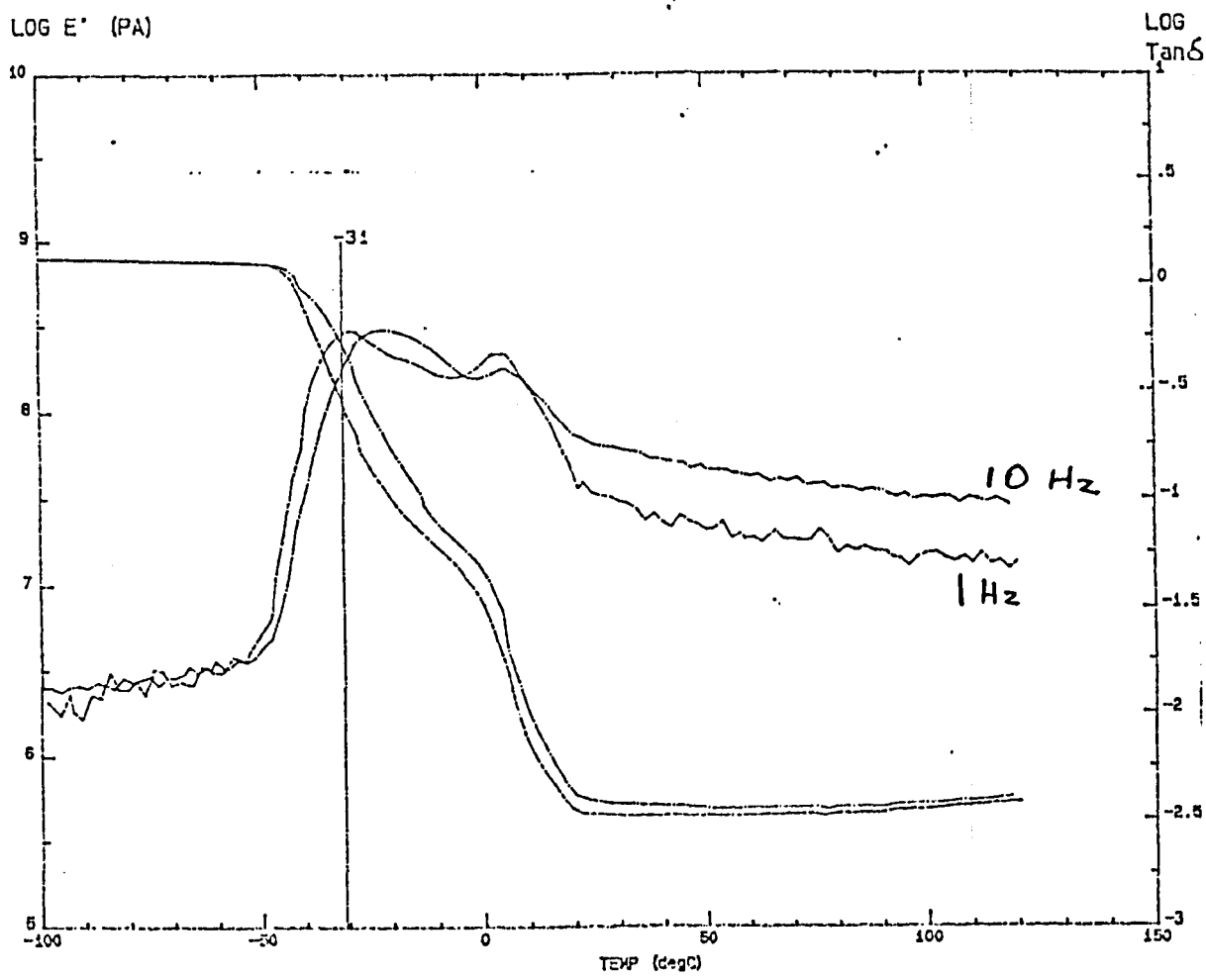
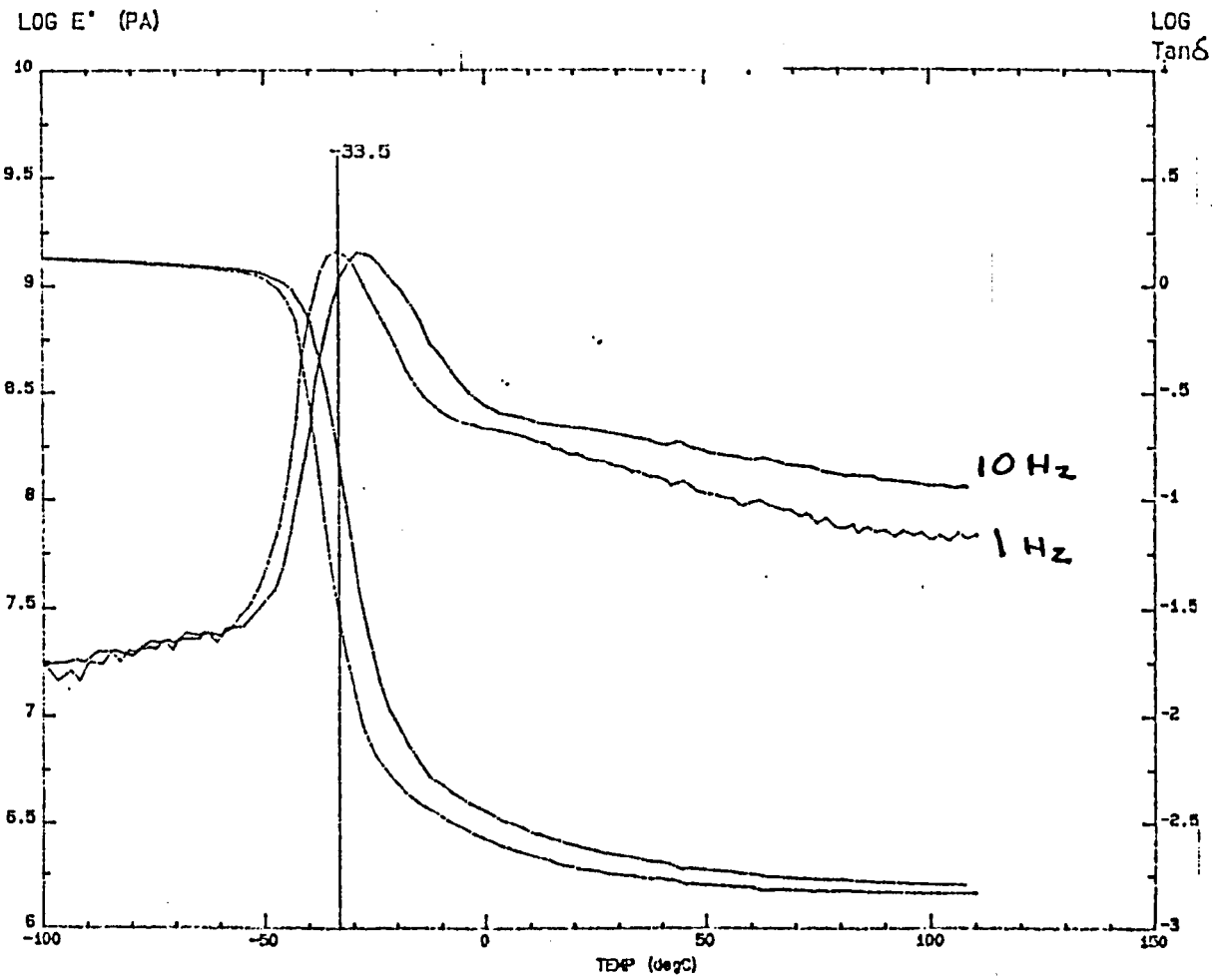


FIGURE 6 DMTA TRACE OF FORMULATION X1 AFTER HIGH HUMIDITY AGEING FOR A PERIOD OF 1 YEAR AND SUBSEQUENT DRYING

measured after the film had been dried



6.3 DMTA TEST RESULTS

The transitions recorded were taken from the DMTA traces and are the points of maximum Tan δ

TABLE 4 TRANSITION TEMPERATURES

formulation	initial	aged wet	aged dry
X1	-29.5	-27.5/2.5	-29
X2	-26	-26/5	-26.5
X3	-27.5	-28/5	-27.5
X4	-27.5	-27/3	-28
X5	-25.5	-26/5	-26.5
X6	-24.5	-26/3	-25
X7	-30	-29/3	-30
X9	-26.5	-26/5	-26

The results under the column 'aged wet' show the temperatures of the two transitions recorded for the sample.

6.4 DISCUSSION

Earlier work on the use of DMTA on polysulfide LP based sealants had concentrated on the effects of individual formulation ingredients on E and Tan δ (51, 52). Whitehouse used DMA to predict sealant behaviour (53), (the DMA is substantially similar to the DMTA). Other workers had used DMTA to study the effects of water penetration into the polymer matrix (54, 55) or to characterise the polymers and their performance (56).

Other workers used thermo/mechanical properties (DSC and stress/strain relationships) to expand theories relating to compatibility (57), yield stress (58), and cross - link density (59).

The DMTA traces of the unaged samples show relatively simple traces with easily defined glass transitions (Tg), as defined by maximum Tan δ, between -20 and -30°C. The author had previously found a relationship between polymer content and Tg in commercial sealants (60) as shown in figure 7. This was found to hold true for the experimental formulations used here and shown in figure 8, in that there is a linear relationship between Tg and polymer content, the Tg increasing with decreasing polymer concentration. The Tg was found to be independant of total binder (polymer + plasticiser), but dependant on plasticiser concentration. This would indicate a lack of plasticisation as the addition of plasticiser would be expected to lower the Tg.

The relationship between Tg and polymer concentration can be seen on the plot of Tg versus polymer content on the unfilled systems (figure 9). The change in Tg however is less than with the test sealants containing filler.

The aged samples showed little evidence of embrittlement or softening, in that little change in the glass transition (Tg) or the modulus/temperature curve was noted between the initial value and the aged value.

FIGURE 7 SHOWING THE EFFECT ON Tg OF VARYING THE POLYMER CONCENTRATION

based on commercial systems. Using the 1Hz values.

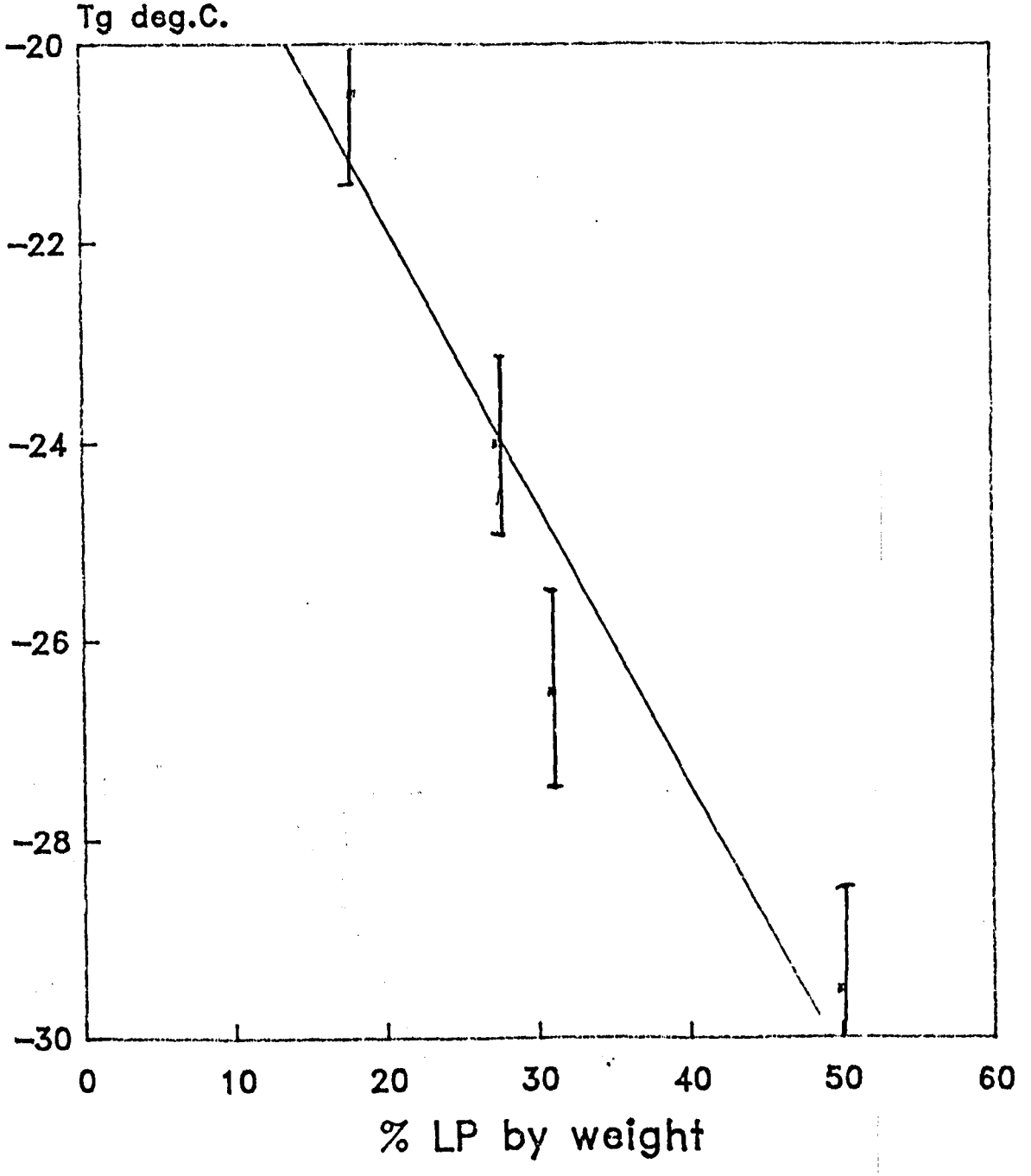


FIGURE 8 SHOWING THE EFFECT ON Tg OF VARYING LIQUID CONCENTRATIONS

using the filled systems as described in tables 3 and 3a section 5

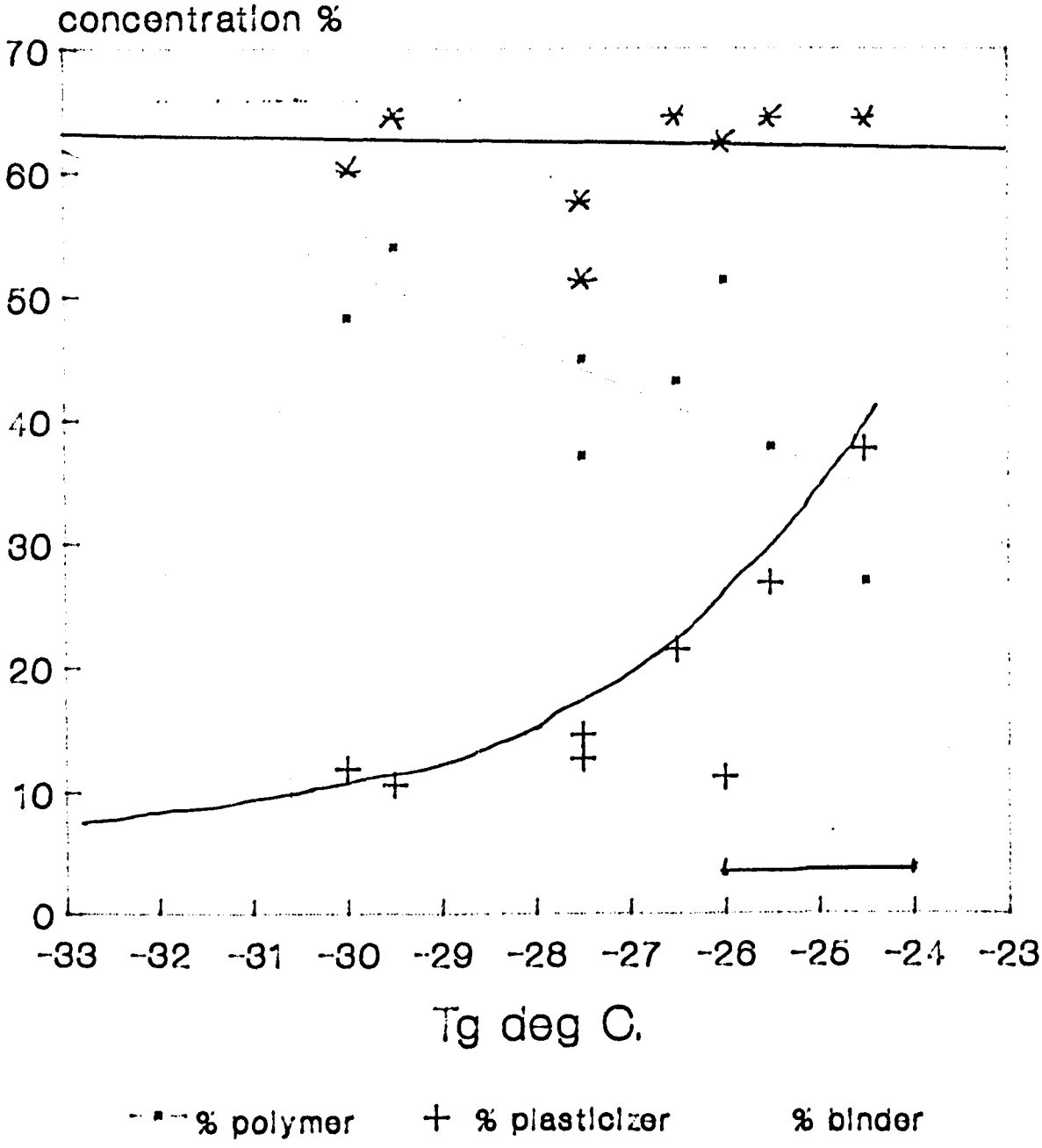
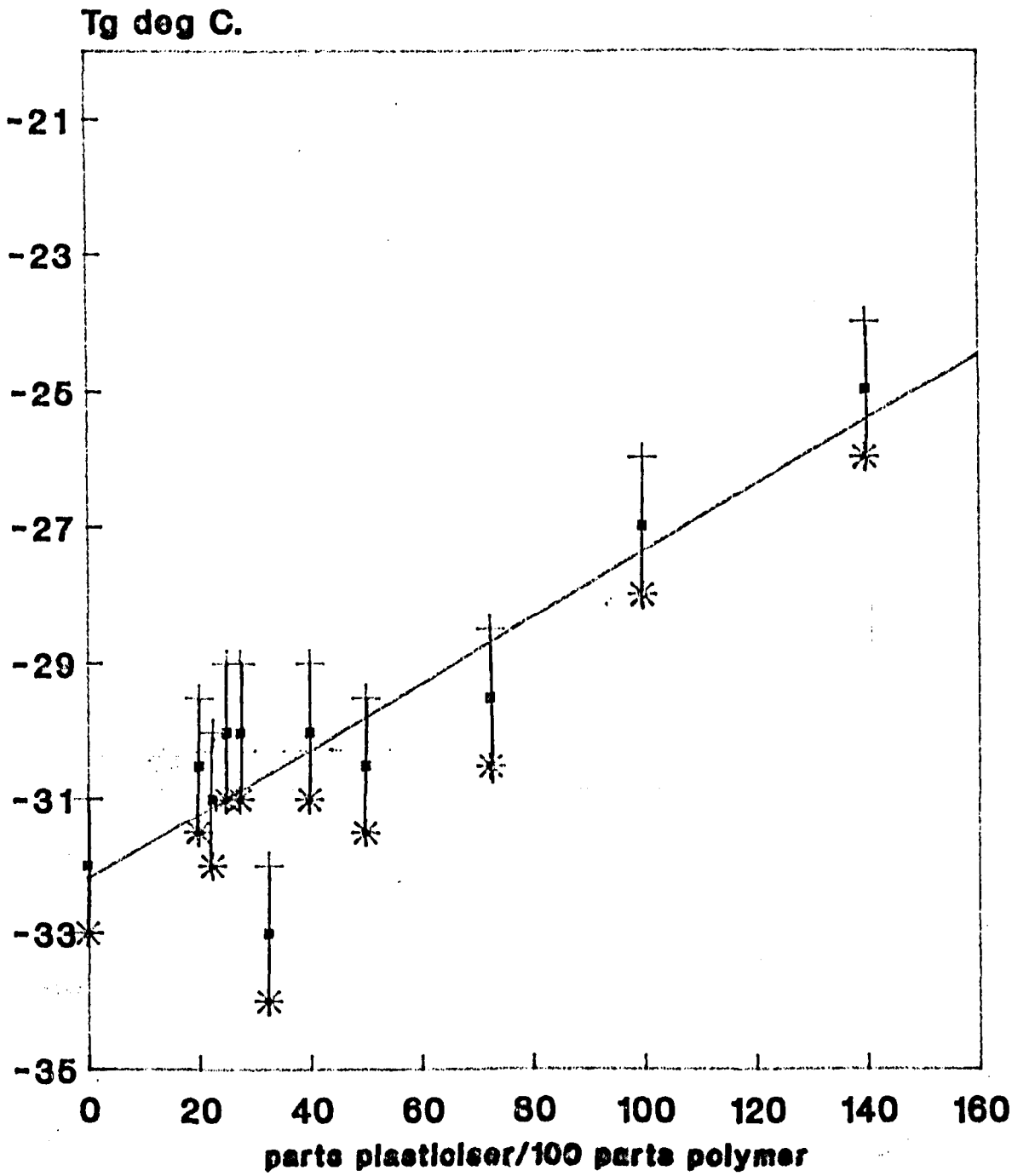


FIGURE 9 SHOWING THE EFFECT ON Tg OF POLYMER / PLASTICISER VARIATIONS

using the unfilled systems, no filler or pigment used



Embrittlement would normally be indicated by an increase in Tg, and age hardening by an increase in modulus.The absence of embrittlement and hardening is is not entirely unexpected on account of the well known durability of polysulfides in construction sealants (61). There was however a secondary transition noted at approximately $+5^{0}C$.

After drying the films at $45^{0}C$ the secondary transitions disappeared, indicating that they were associated with water diffusing into the sealant film, which was present as droplets in the sealant matrix rather than being chemically bound or reacted. The water can therefore readily diffuse out of the film when the conditions are correct. Examination of these films and of the films used in the water uptake experiment indicated porosity of the films after drying as shown in plate 3.

It was considered that the porosity was the result of the diffused water forming discrete droplets and forcing the polymer matrix apart. The polymer would, under the conditions of test, stress relax to take up its distended form. On drying at a lower temperature there is no stress applied to force the system to return to its original profile. Therefore as the water is removed from the system voids are formed.

These findings indicate that the plasticiser does not perform as a true

plasticiser, in that the Tg would be expected to decrease with increasing concentration, but more as a diluent. Secondly the water diffusing into the film was only loosely bound.

An alternative explanation for void formation has been advanced by Hanhela (62) who suggested an acid reaction with the filler forming carbon dioxide, which then gave rise to the voids. In order to examine this claim the weight of the films was noted. If the theory is true, then a permanent weight loss would result related to the calcium carbonate filler levels in the system. The weight of some of the films after drying for 12 months at 50°C compared to their original weight is given in the table 5 below.

If the weight loss was all attributed to carbon dioxide evolution this would represent approximately 0.2 litres of gas at S.T.P. As a comparison the calcium carbonate present in the film of formulation X4 which contains the most calcium carbonate has a potential carbon dioxide evolution volume of 918 litres.

As can be seen in table 6 there is little relationship between calcium carbonate concentration and weight loss. Taking formulation X7, the time to reach equilibrium in the water/mass uptake experiment of section 9 was 144 days, which is an average of 0.003 g day^{-1} or 0.0001 g cm^2 day^{-1}.

From gas permeation data, Argon transmission (having the nearest molecular

mass to CO_2 for which data is available) is given as 0.05 g m^2day^{-1} for a 1mm thick film at 23°C. This relates to 0.000005 g for a 1cm^2 area, or 1/20th that expected from loss of CO_2 only if all the calcium carbonate was reacted. Some correction must be made for the temperature of testing being 60°C whereas the permeation rates are given at 25°C. The only data found was for water permeation which suggests a 5X rate increase from 23°C to 60°C. Thus the small quantity of CO_2 generated would diffuse from the sealant with ease, there would be no cause for CO_2 void formation.

TABLE 5 WEIGHT LOSS OF SEALANT ON AGEING

(averages of three films)

	initial weight	final weight	Δweight
X4	11.982	11.581	0.401
X5	10.692	10.324	0.368
X7	10.829	10.425	0.404
X8	12.550	12.068	0.482
X9	9.669	9.336	0.337

TABLE 6 CALCIUM CARBONATE CONCENTRATION V WEIGHT LOSS ON AGEING

COMPOUND	CALCIUM CARBONATE %	WEIGHT LOSS %
X4	34	0.401
X5	25	0.368
X7	28.5	0.404
X8	30	0.482
X9	25.5	0.337

Whilst this still leaves the potential for void formation it still does not explain why the mass losses are similar for different formulations.

A further explanation could possibly be derived based on the work by Lefebvre (160) who showed that moisture diffusion was affected by the induced strain in the adhesive.

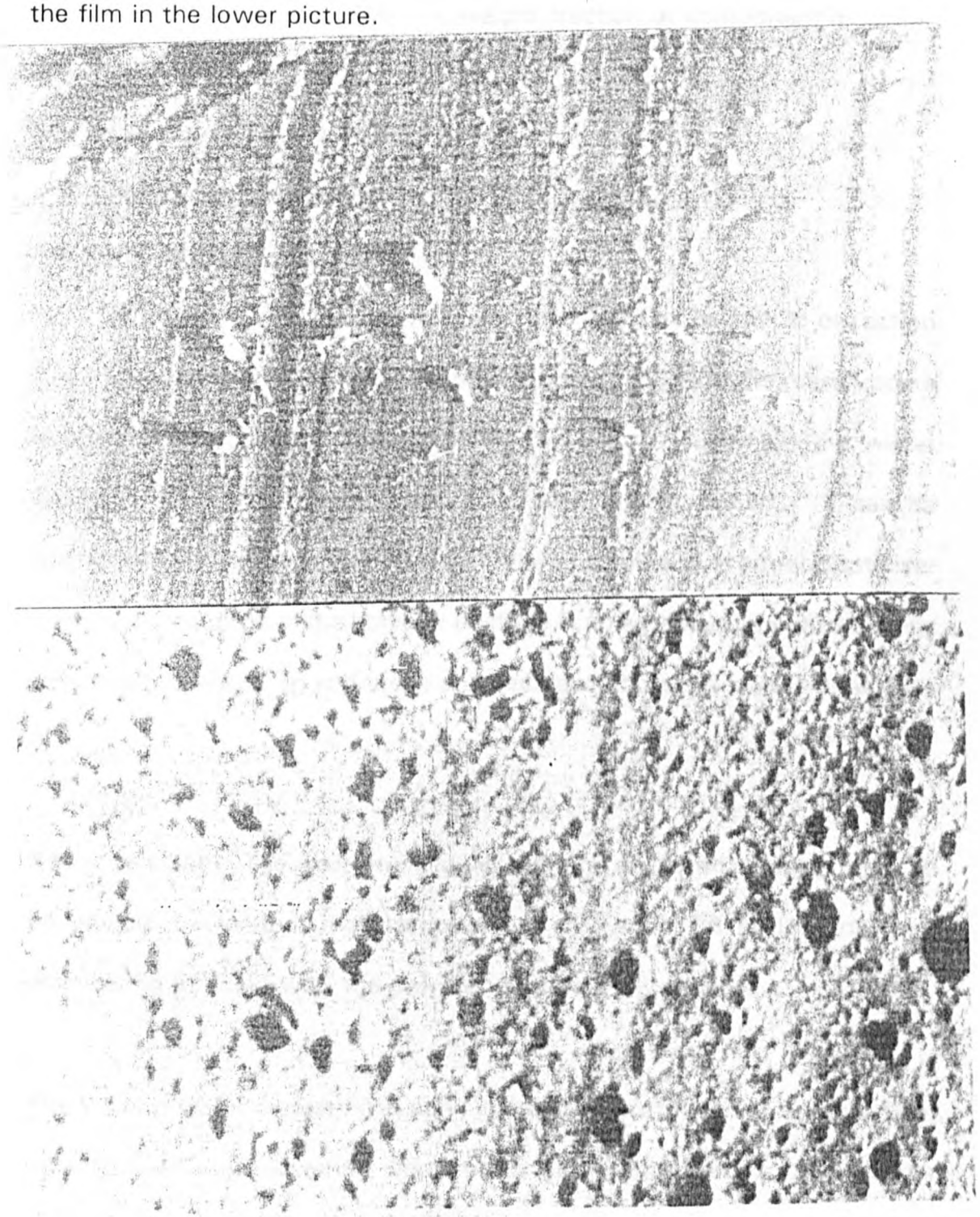
The solubility of the plasticiser and water in the polymer can be tested using the theory that where true solution takes place for a two component system then the resultant Tg can be calculated using the Fox equation (159) :-

$$\frac{1}{Tg} = \frac{W_a}{Tg_{(a)}} + \frac{W_b}{Tg_{(b)}}$$

PLATE 3 PHOTOMICROGRAPH OF THE SEALANT FILM

the upper picture shows before environmental ageing

the lower picture shows after environmental ageing. Note the porosity of the film in the lower picture.



where $Tg_{(a)}$ = Tg of pure component a

$Tg_{(b)}$ = Tg of pure component b

Wa = weight fraction of component a

Wb = weight fraction of component b

The Tg of the polymer = -32°C (241°K)

The Tg of water = 130°K

The Tg of plasticiser = 198°K

From the polymer/plasticiser blends described in tables 3a and 3b of section 5.1.1 this should yield Tg's between -87 and -95.8°C. For the mass uptake of water (see table 10 section 8) the Tg values (assuming the water dissolves in the polymer) should lie between -18 to -56.8°C. It can be concluded from these calculations that little true solution of either plasticiser or water takes place in the polymer as there is no agreement between these calculated values of Tg and those observed and shown in table 4 of section 6.3.

As the calculated Tgs were much lower than the observed values it must be concluded that neither the plasticiser nor the water are performing their plasticising function with the polymer as previously thought.

The view of water clustering in polymers has been studied by Jacobs (164) who showed that clustering would occur above 30%R.H. for the polymer system studied. No critical humidity has been investigated for polysulfides.

7 DIFFERENTIAL SCANNING CALORIMETER

7.1 DESCRIPTION OF D.S.C.

Differential Scanning Calorimetery (D.S.C.) involves heating a small sample of material and measuring the small difference in rates of heating in comparison with a reference sample. For these experiments the reference sample was an empty sample holder.

Heat differences can be either exothermic or endothermic. It is thus possible to define points of transition relating for example to Tg, melting of crystals, or dissociation. It was envisaged that this would confirm the melting of captured water in the sealant as predicted by DMTA.

The original equipment used was a Mettler DSC supplied by Fisons Equipment Ltd., whilst later work was carried out on a Stanton Redcroft DSC 700 supplied by Polymer Laboratories Ltd.

7.2 EXPERIMENTAL AND RESULTS

The technique used was to weigh accurately approximately 10 mg of sealant taken in one piece from the films used in the DMTA experiments. The measuring head was cooled with liquid nitrogen to below the start

temperature. A heating rate of 10°C per minute was used.

A sample of the film (formula X1 of table 3a section 5.1.1) that had been aged for 1 year in the environmental cabinet, together with a sample of cure paste were tested initially. Because of the extra transition at 2.5 to 5°C found during the DMTA analysis (figure 5 section 6.3) a calibration thermogram using water was prepared. The position of the ice/water transition could then be compared with any transition in the sealant thermogram.

The film, water and a cure paste thermograms are shown in figures 10,11 and 12, with further examples in appendix B.

It should be pointed out here that due to observed results obtained on the sealant samples using both DMTA and DSC, the tests were repeated using the unfilled systems in an attempt to examine the polymer - plasticiser interaction without the influence of the fillers. The DMTA results are shown in figure 9.

The D.S.C. results confirmed the secondary transition was associated with the diffused water, the calibration against water giving positive identification of the peak, in that the transition at 0°C to 6°C matched in both thermograms. This reinforced the argument that the water was present in discrete droplets within the film matrix in that there was no boiling or

FIGURE 10 DSC TRACE OF WATER

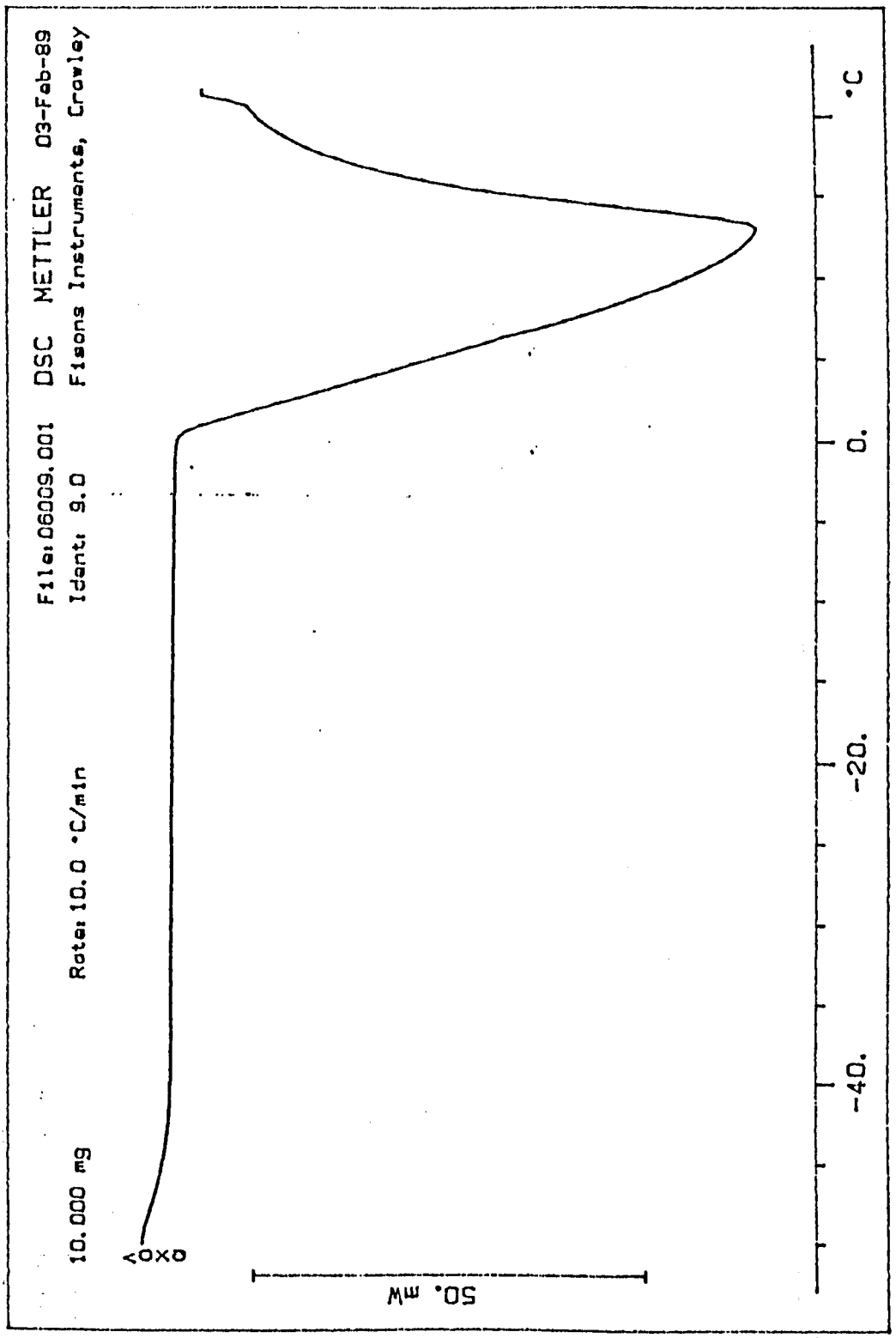


FIGURE 11 DSC TRACE OF CURATIVE

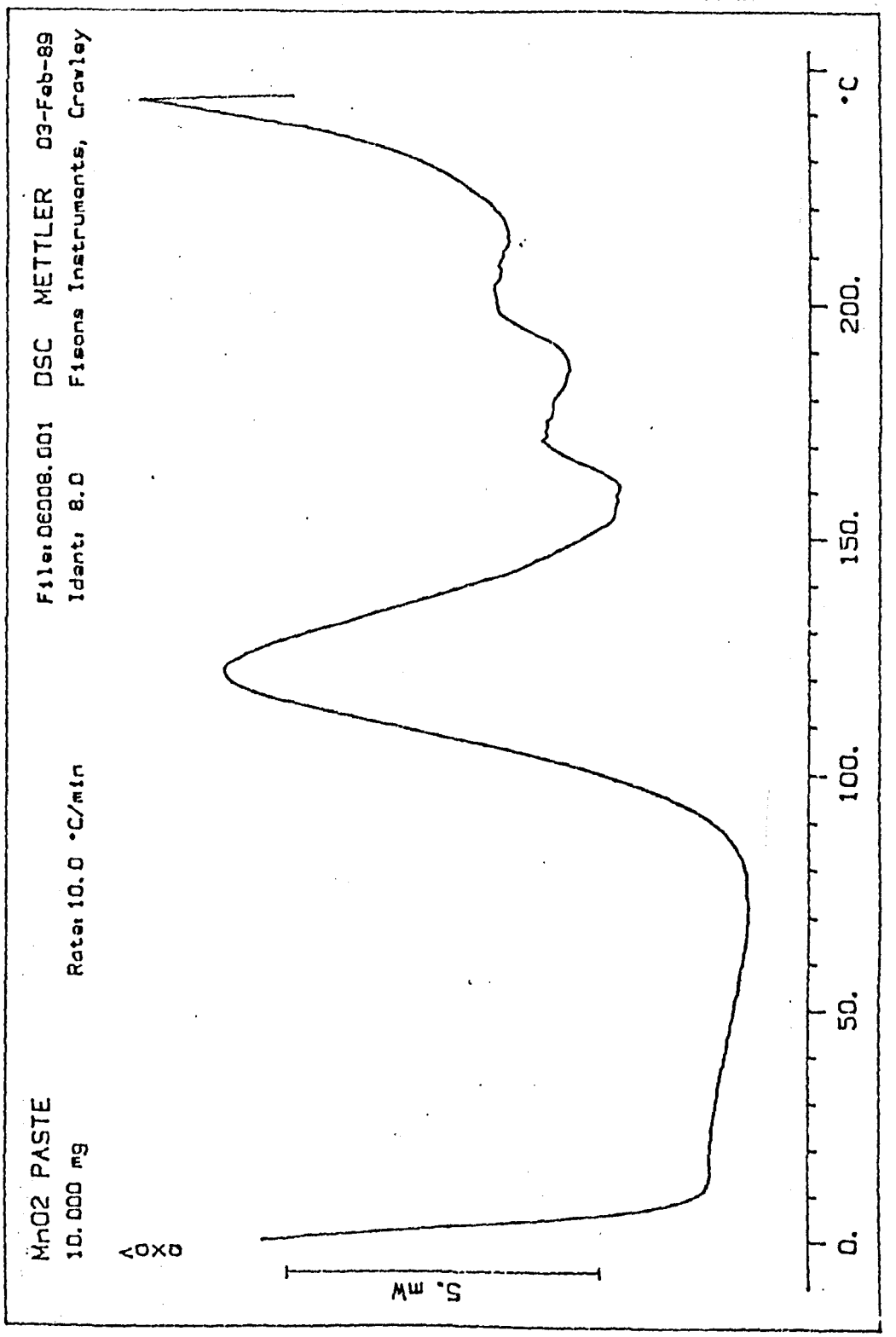
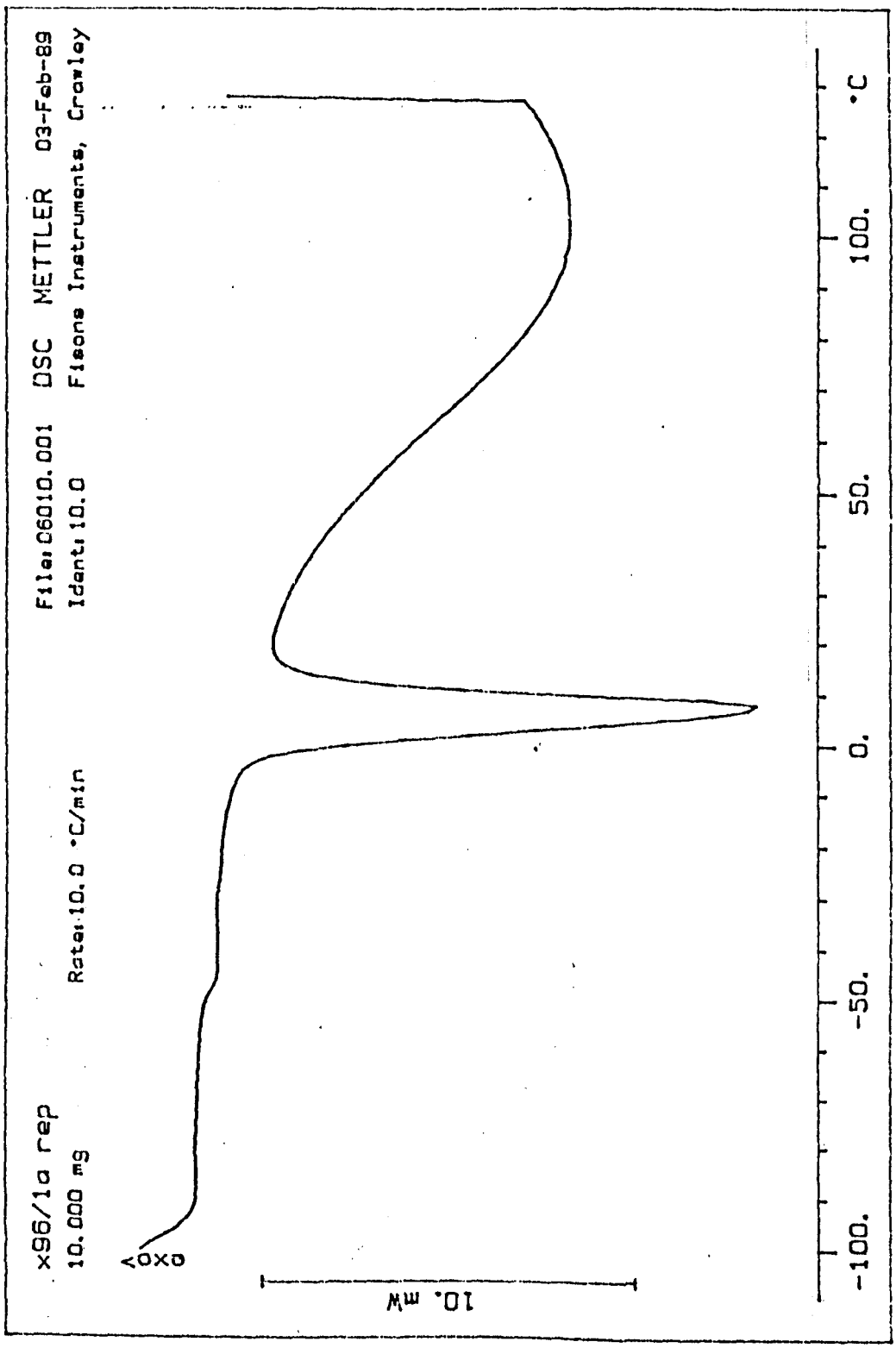


FIGURE 12 DSC TRACE OF TEST FILM FORMULATION X1

measured immediately after humidity ageing

for comparison with figure 5



melting point shift.

During this test programme it was decided to run a D.S.C. on the cure paste as it had been suggested that the curing paste may give secondary reactions when heated through the Tg. Although transitions occurred they were not present on the sealants thermograms.

The traces of the unfilled systems showed a transition at approximately 10°C. This was later found to be associated with some changes in the plasticiser not detected on the DMTA. A DSC on the plasticiser alone confirmed this. As this transition did not appear to affect examination of the sealant properties no further action was taken.

8 MASS UPTAKE EXPERIMENTS

8.1 WATER UPTAKE BY SEALANTS

That water diffuses into polymer films is not in dispute. What is not agreed is what role the diffused water plays in bond deterioration between sealant and glass in insulated glass units. The peculiarities of water diffusion into polymer films have been studied for some time in paint films (63) leading to debate on the nature of water itself (64). In the latter case Drinkard describes the hydrogen-oxygen-hydrogen angle as being 104° and this together with the ability of water to behave ionically,

$$H_2O + H_2O \rightarrow H_2O^+ + OH^-$$

is used to explain some of the behaviour of water as a solvent.
Similarly the ways in which water can be present in a system is explained. Micheals has studied the effect of water on barrier films and indicated that pigmentation could markedly influence the diffusion of water into paint films.

The concept of water diffusion being related to the rate of adhesion failure has been explored by other workers with respect to structural adhesives, and is dealt with in the book "Durability of Structural Adhesives" edited by A. J. Kinloch. (70) The issue is further explored in "Polymer Permeability" edited by J. Comyn (71), and in his article "The Interaction of Water with Plastics and Rubbers" (72). The effect of formulation on diffusion has been

explored in coatings (73) to show that care was needed in defining the requirements of the product especially where long term service life was required.

Moloney used the diffusion coefficient in her experiments on adhesion stability of epoxy adhesives (67) , whilst Gick examined the diffusion of aviation fuel and water in polysulfide based sealants used in the aircraft industry (68). These latter compounds are cured using soluble chromate salt curing agents particularly sodium and ammonium dichromate.

As Gick found that there was a relationship between the residual water soluble fraction in a sealant and its diffusion coefficient the experiments in this work were extended to investigate the relationship between the water soluble contents of the curing agent and the diffusion coefficient of the sealant cured with that curing agent.
The contribution of the curing agent to volume swelling had been examined by earlier workers (69, 62).

The relationship between adhesion and diffusion of plasticiser into the sealant has not been investigated, and neither has the combination effect of water and plasticiser diffusion.

8.2 THEORY OF DIFFUSION

Fick in 1855 related the heat transfer by conduction to the diffusion of a substrate through unit area of a section of an isotropic substance and showed this by the mathematical relationship

$$F = -D \frac{\partial c}{\partial x} \qquad 1$$

Where F = The rate of transfer per unit area of section or flux

c = concentration of diffusing substance

x = the space co-ordinate measured normal to the section

D = the diffusion coefficient

The minus sign occurs because diffusion progresses in the opposite direction to that of increasing concentration. If F and c are expressed in the same units then D is expressed in $(length)^2(time)^{-1}$ for example m^2s^{-1}

For dilute solutions D is reasonably constant whereas in other systems D may vary with concentration. Equation 1 is referred to as Fick's first law of diffusion.

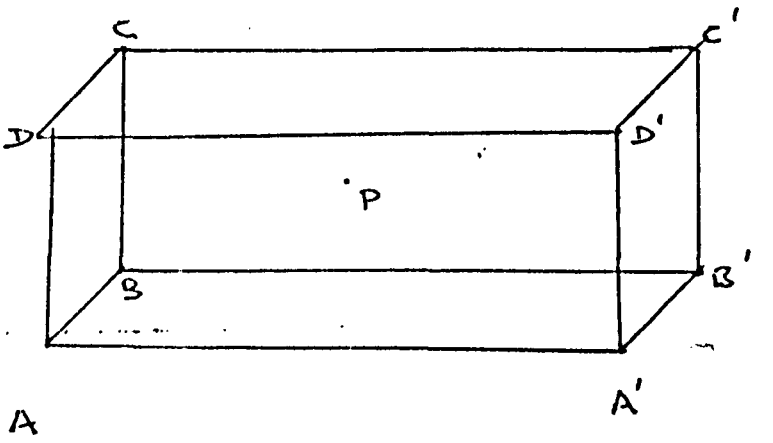
Consider an element of volume in the form of a box shape which has edge length 2dx, 2dy, 2dz. A point P is at the centre of the volume element, co-ordinate P(x,y,z) as shown in figure 13.

If the faces perpendicular to the x axis are ABCD and A'B'C'D' and the concentration of diffusant at P is c, and if there is a flux gradient F/∂x in the x direction then the actual flux at ABCD is given by

$$(Fx - (\partial Fx/\partial x))dx \qquad 2$$

then the material entering that face in the plane x - dx is

$$4dydz(Fx - (\partial Fx/\partial x))dx \qquad 3$$



$A - A' = 2dxc$
$A - D = 2dy$
$C - D = 2dz$

figure 13

similarly that leaving the face A'B'C'D' is equal and opposite

$$4dydz(Fx + (\partial Fx/\partial x))dx \qquad 4$$

Combining the two values by summation, that is equations 3 and 4, to determine the increase of diffusant due to diffusion in the x direction gives

$$Rx = -8dx\ dy\ dz\ (\partial Fx/\partial x) \qquad 5$$

Similar equations can be derived for the faces CDC'D' to ABA'B' and AA'DD' to BB'CC'

$$Ry = -8\ dx\ dy\ dz\ (\partial Fy/\partial y) \qquad 6$$

$$Rz = -8\ dx\ dy\ dz\ (\partial Fz/\partial z) \qquad 7$$

Taking concentration into account the rate at which the diffusant increases in the element can be given by

$$8\ dx\ dy\ dz\ \partial C/\partial t \qquad 8$$

$$\text{hence} \quad \frac{\partial C}{\partial t} = \frac{\partial Fx}{\partial x} + \frac{\partial Fy}{\partial y} + \frac{\partial Fz}{\partial z} \qquad 9$$

By differentiating equation 1 we obtain

$$\partial Fx/\partial x = -D\partial^2 c/\partial x^2 \qquad 10$$

Hence if the diffusion is constant through the three faces we get

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right) \qquad 11$$

This is known as Ficks second law of diffusion.

If the diffusion is along the x axis only i.e. there is a gradient of concentration in the x direction only equation 11 can be simplified to

$$\partial C/\partial t = D\partial^2 C/\partial x^2 \qquad 12$$

Diffusion is treated mathematically by Crank in his book "The Mathematics of Diffusion" (65), where he expands the arguments for diffusion in different circumstances. The interest in this work is for diffusion in a plane sheet, and Crank's solution yields equation 13

$$C = C_o \sum_{n=0}^{\infty} (-1)^n \frac{erfc(2n+1)\,l-x}{2\sqrt{Dt}} + C_o \sum_{n=0}^{\infty} (-1)^n \frac{erfc(2n+1)\,l+x}{2\sqrt{Dt}} \qquad 13$$

where C_0 = concentration at time 0

erfc is the error function

l = length of diffusion path

However this is only suitable for short time determinations.

The expression $2\sqrt{Dt}$ is known as the diffusion path length

8.3 DIFFUSION IN A PLANE SHEET

When considering the case of a plane sheet with surfaces at -l and +l (where l is half the total sheet thickness) i.e. if the liquid concentration in the sheet where $-l < x < l$ is initially zero the surface concentration is C_1 then the concentration C in the sheet at time t can be written as equation 14

$$\frac{C}{C_1} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left\{\frac{-D(2n+1)^2 \pi^2 t}{4l^2}\right\} \cos \frac{(2n+1)}{2l} \pi x \qquad 14$$

when concentrations are not equal then equation 15 is applicable

$$C = C_1 + (C_2 - C_1) \frac{x}{l} + \frac{2}{\pi} \sum_{1}^{\infty} \frac{C_2 Cosn\pi - C_1}{n} Sin \frac{n\pi x}{l} Exp\left\{\frac{-Dn^2 \pi^2 t}{l^2}\right\} + \frac{2}{l} \sum_{1}^{\infty}$$

$$\sin \frac{n\pi x}{\pi} \exp\left\{\frac{-D\pi^2 n^2 t}{l^2}\right\} \int_0^1 (x^1) \sin \frac{n\pi x^1}{l} dx^1 \qquad 15$$

however this is not used in this work

If Mt and M∞ represent the amount of diffusant entering into the sheet at time t and at infinite time t∞ respectively equation 15 can be used to represent the fractional mass uptake Mt/M∞ (equation 16)

$$\frac{Mt}{M\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left(\frac{-D(2n+1)^2\pi^2 t}{4l^2}\right)$$

16

If D is constant then Mt/M∞ will be proportional to $2(Dt/l^2)^{1/2}$ in the early stages.

Thus the diffusion coefficient can be found by following the mass uptake of water into a film until equilibrium is reached and then plotting Mt/M∞ against $t^{1/2}$.

The use of the diffusion coefficient may then be a useful guide to predicting the rate at which water enters sealants in insulating glass units. Attempts have been made to use the mathematics of diffusion to calculate service life of insulated glass units (66), although the relationship between permeability, diffusion and solubility, simplified to P = DxS has not been explored.

28.4 DETAILS OF WATER UPTAKE EXPERIMENT

8.4.1 PRELIMINARY EXPERIMENTS

In the first instance, a trial run was made to establish the reproducibility of results. The test runs were made on films cast of formulations X1 and X7. Ten films of each formulation were subjected to the standard test environment of 60°C and 95% R.H. and the weight gain noted, see table 7 below. The results suggested that reproducibility was good, and it was concluded that for the determination of the diffusion coefficient proper it was only necessary to use four samples per formulation.

TABLE 7 Initial Trial Experiments on water uptake

sample X1	average wght.(gms)	S.D.	average uptake %
initial	12.8283	0.98	-
7 days	13.6732	1.065	6.6
17 days	14.4354	1.031	12.5
24 days	14.3704	1.268	12.0
72 days	16.3680	1.581	27.6

Sample X2	average wght.(gms)	S.D.	average uptake %
Initial	12.9419	1.534	-
7 days	13.6929	1.265	5.8
14 days	14.3823	1.368	11.1
24 days	14.9355	1.356	15.4
72 days	16.5321	1.450	27.7

8.4.2 MASS UPTAKE EXPERIMENT

For each formulation, films were prepared by first carefully mixing for 10 minutes the base and curative in the correct calculated ratio, as defined for the sealants of section 5. The sealant was transferred onto a release paper forming a pyramid shape. Care was taken to avoid trapping air during the transfer.

A metal former 2mm thick and with internal dimensions of 100mm x 100mm was placed round the sealant and a second release paper placed over the top of the pyramid. The sandwich thus formed was placed between two sheets of 10mm glass and the whole assembly pressed flat. The assembly was left to cure overnight at 23°C and 50% R.H. before the film was exposed to the air, by removing the top layer of glass and release paper, and left to cure for a further 6 days at laboratory conditions of 23 °C and 50%R.H.

The films were trimmed of any non-uniform edges to yield films of approximately 100mm x 20mm x 2mm. The initial thickness was checked with a micrometer. Four such films of each sealant formulation were prepared.

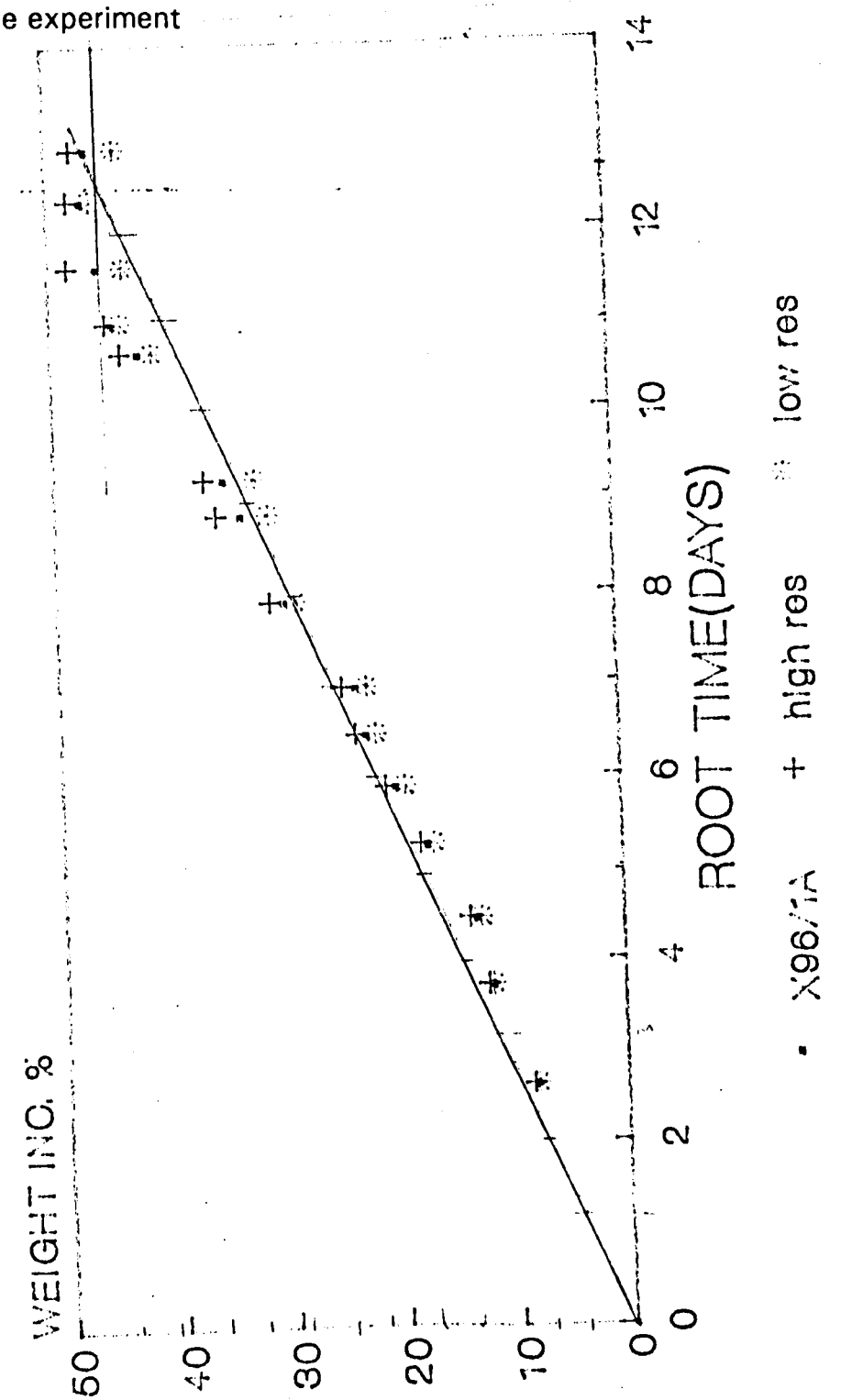
The four films were then weighed accurately before being placed in the environmental cabinet, on stainless steel open mesh shelves to ensure all-round exposure. The films were weighed at various intervals and the weight increase calculated. The weight increase (average) was plotted against root time until equilibrium was reached. A typical plot of mass uptake is shown in figure 14. The highest and lowest result is also shown for comparison.

Further plots are shown in appendix C.

The equilibrium mass uptake was taken as that point when three or more values remained constant. All these points are not necessarily included in the graphs. It should also be noted that the X axis is root time and therefore the period of equilibrium was a significant time lag following the Fickian increase noted at the beginning of the experiment.

FIGURE 14 WATER UPTAKE PLOT FOR X1 IN WATER VAPOUR AT 60°C.

Graph showing the weight gain of a test film plotted against square root of the time in days. Testing was continued until equilibrium was attained as shown by constant weighings. The three values represent the total variation within the experiment



8.5 RESULTS OF WATER UPTAKE EXPERIMENTS

After weighing the samples the time to reach saturation ($t\infty$) was noted together with the maximum water uptake ($M\infty$),which ranged from 45 to 100%, from figure 14.

It can be shown from equation 16 that the time $t_{1/2}$ at which $M_t/M\infty = 0.5$ is related to the diffusion coefficient by

$$D = 0.049/(t_{1/2}/l^2)$$

The calculated values of the diffusion coefficient can then be compared with the variations in formulation. This was to investigate which formulation ingredient, polymer, plasticiser or filler had the greatest influence on diffusion

These comparisons are listed in table 9, and displayed diagrammatically in figures 15 to 17. It was noted during the testing that formulation X6 having the highest plasticiser/polymer ratio was exuding plasticiser. The graphs and subsequent discussion therefore omit reference to this formulation.

TABLE 8 MASS UPTAKE AND DIFFUSION COEFFICIENT OF WATER IN CURED SEALANT

formulation	t(∞) days	equilibrium mass uptake %	$t^{1/2}$ days	D(calculated) x10^-14 m^2s^{-1}
X1	36	45	16	1.61
X2	169	63	42.25	1.37
X3	169	52	42.25	1.37
X4	196	50	56.25	1.03
X5	169	100	73.96	0.78
X6	81	63	25	2.31
X7	144	70	36	1.61
X8	196	58	56.25	1.03
X9	210	65	49	1.18

TABLE 9 VARIATION OF DIFFUSION COEFFICIENT WITH FORMULATION VARIABLES

	(Po%) Polymer	(Pl %) Plasticiser	(%) Filler	PVC	Ratio Po/Pl	Diff coeff x10^-14 m_2s_{-1}
X1	54	11	32	19	5	1.61
X2	51	11	34	21	4.5	1.37
X3	45	13	38	24	3.5	1.37
X4	37	15	44	28.5	2.5	1.03
X5	38	27	32	19	1.4	0.78
X6	27	38	32	19	0.714	2.31
X7	48	12	36	22.5	4	1.61
X8	41	14	41	26	3	1.03
X9	43	21.5	32	19	2	1.18
X10	32	32	32	19	1	----

FIGURE 15 DEPENDENCE OF WATER DIFFUSION COEFFICIENT ON POLYMER CONTENT

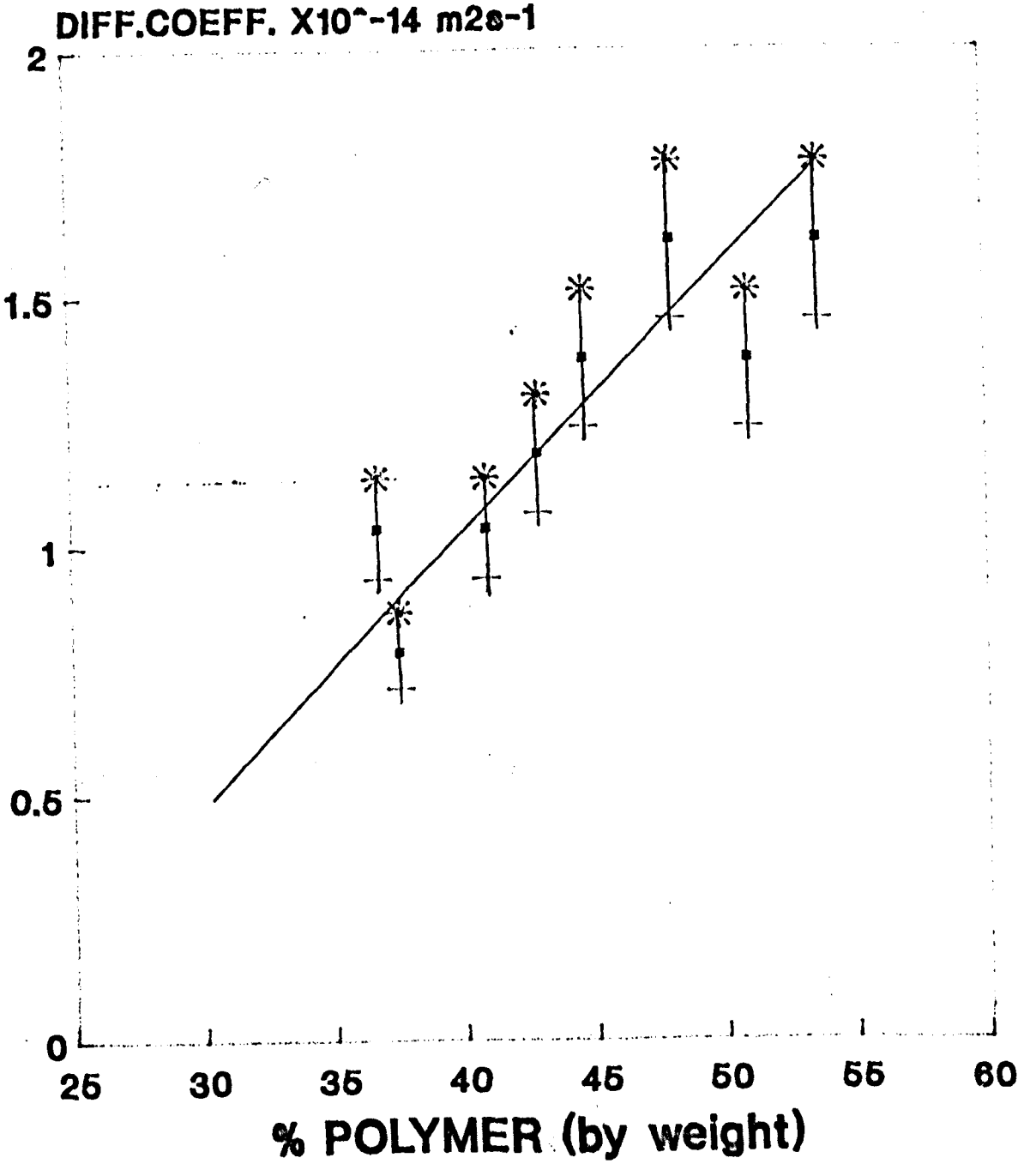


FIGURE 16 DEPENDENCE OF WATER DIFFUSION COEFFICIENT ON PLASTICISER CONTENT

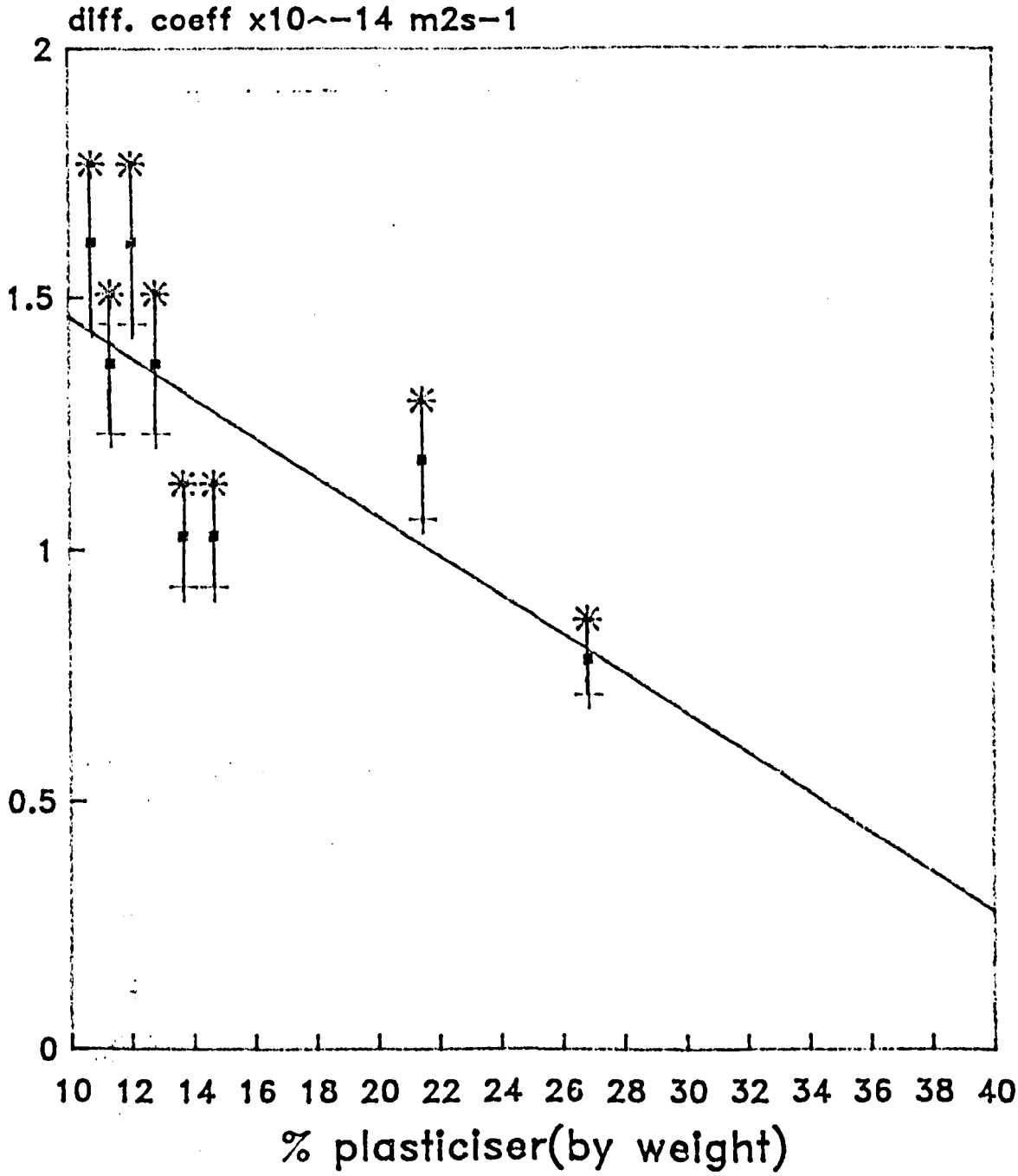


FIGURE 17 DEPENDENCE ON WATER DIFFUSION COEFFICIENT ON FILLER LOADING

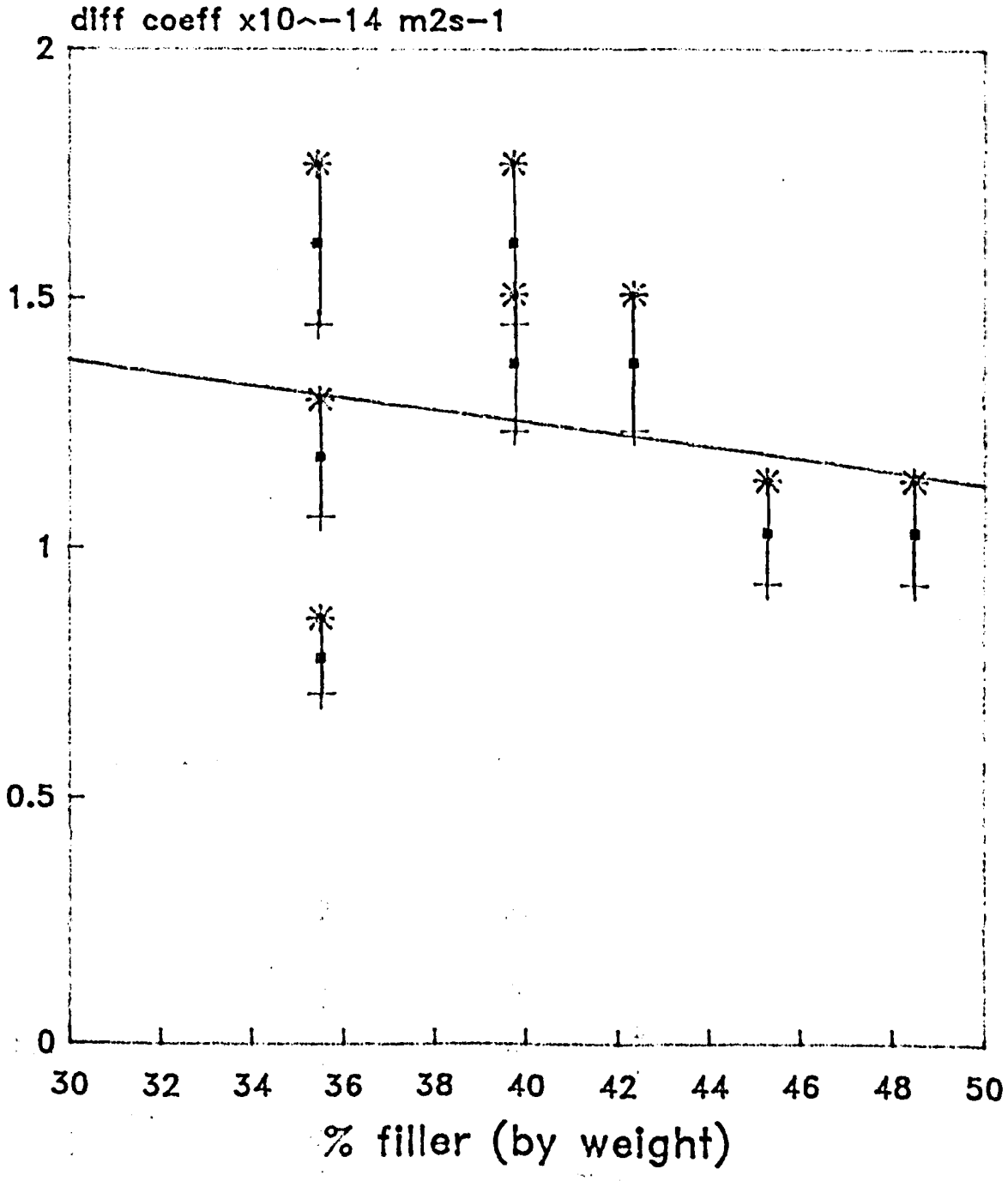


Figure 15 shows that there is an increase in diffusion coefficient with polymer content, whereas figure 16 shows the reverse is true, although less pronounced, for plasticisers. Figure 17 shows that the filler loading has little effect on water diffusion coefficient.

The diffusion coefficient is plotted against polymer/plasticiser ratio in figure 18. This shows that D increases with the amount of polymer as previously noted. It was noted during experimentation, and carrying out the adhesion testing simultaneously, that the two products having the highest levels of plasticiser (X5 and X6) failed adhesively before environmental ageing could commence. Also X5 had the lowest diffusion coefficient of all the systems tested.

Following this, the volume ratio of the main constituents were examined, as opposed to weight ratio used previously.The volume ratio of polymer to plasticiser gives a similar graph as that for the weight ratio, cf figure 18. By using a simple computer programme to calculate the filler volume (commonly referred to as Pigment Volume Ratio or PVC from paint technology), the results of diffusion coefficient against PVC can then be compared. A graph of diffusion coefficient versus PVC shows some scatter (figure 19); a curve has been fitted to the points but a possible alternative interpretation is that the diffusion coefficient remains constant.

FIGURE 18 DEPENDENCE OF WATER DIFFUSION COEFFICIENT ON POLYMER/PLASTICISER RATIO

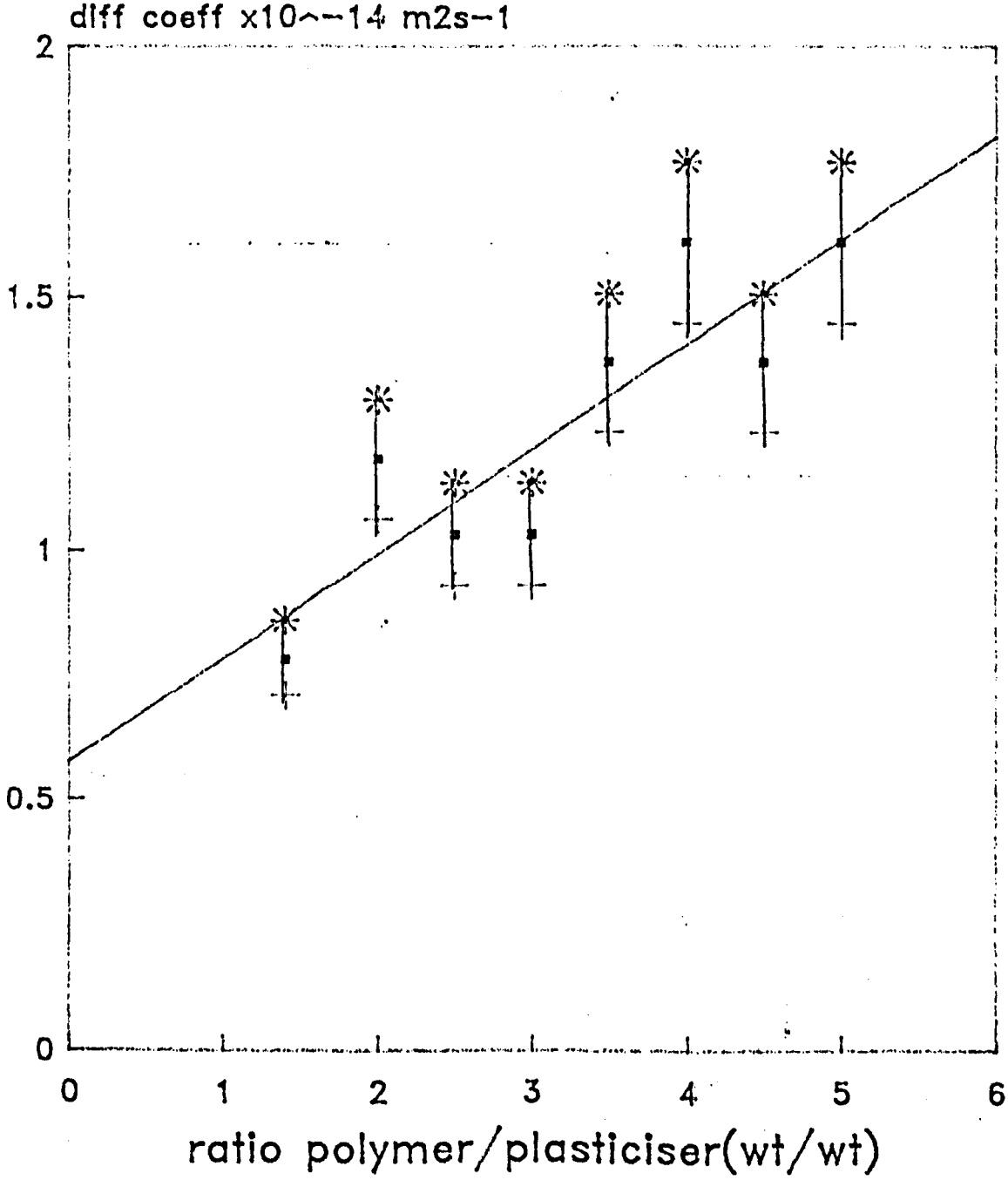
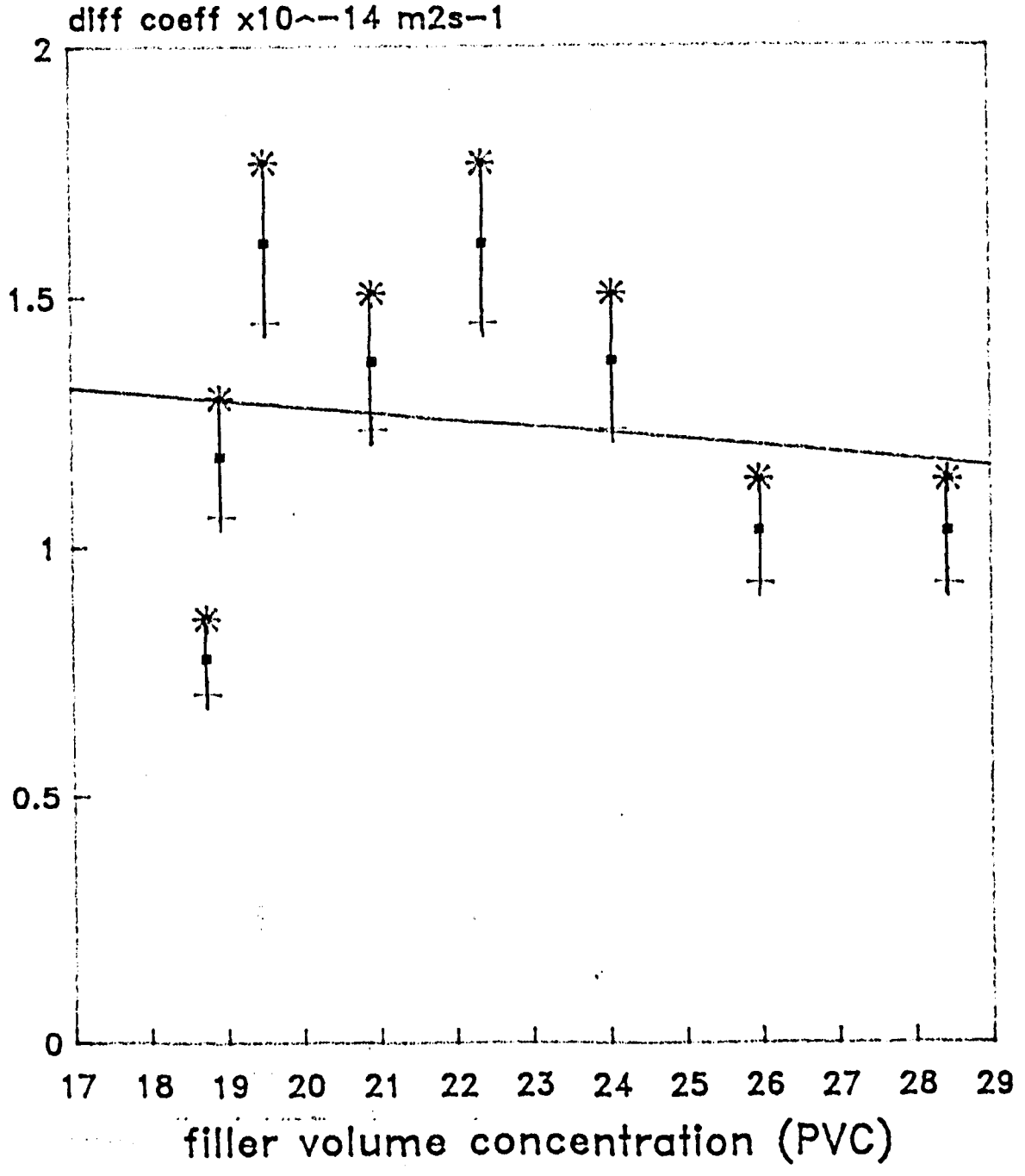


FIGURE 19 PIGMENT VOLUME CONCENTRATION V WATER DIFFUSION COEFFICIENT



8.6 EFFECT OF WATER SOLUBLES IN THE CURING AGENT ON MASS UPTAKE

Formulation X1 (section 5.1.1 table 3) was used to evaluate the effect on the diffusion coefficient of water soluble impurities in the manganese dioxide curing agent; the latter were measured by the cold water extraction method described in section 9.

The films were cast and aged as for the standard diffusion test although for this part of the evaluation the variable was the manganese dioxide curing agent, the base remaining constant. The manganese dioxides were from a number of manufacturers as shown in table 12 section 9.2.

From the mass uptake of water into the films plots of $Mt/M\infty$ against $t^{1/2}$ were made and the diffusion coefficient calculated as described previously.

The results of this experiment are discussed after section 9.

8.7 MASS UPTAKE OF PLASTICISER

The possibility of plasticiser migration was considered worthy of investigation as this could lead to adhesion failure by forming a plasticiser rich layer near to the sealant/glass interface. This could be investigated by surface analysis, see section 10.

Films were cast of formulation X1 and the following polymer/plasticiser mixes cured with the standard curative.

TABLE 10 COMPOUNDS USED FOR PLASTICISER MASS UPTAKE EXPERIMENT

FORMULATION	POLYMER	PLASTICISER
X1	100	20
CONTROL	100	20
A	100	40
B	100	50
C	100	60
D	100	80
E	100	100

The control has the same polymer/plasticiser ratio as sealant X1.

The unfilled systems were used as it was felt necessary to obtain data regarding the movement of plasticiser through the polymer matrix and to use the filled system X1 as a base for comparison.

The method of preparing the films and the film thicknesses are as described in 8.4.2.

After curing the films were measured for thickness and immersed in plasticiser (santiciser 278) and stored at 60°C., which was the temperature of the water in the mass uptake experiments. Care was taken to ensure the films were fully surrounded by plasticiser, such that diffusion could take place from both faces.

The films were removed from the plasticiser at various intervals and the excess plasticiser allowed to drain off. The films were then carefully dried by swabbing with absorbent paper three times, and ensuring there was no residual plasticiser by careful visual inspection, before being weighed. Mass uptake and diffusion was derived via graphical interpretation of the results as described in section 8.5

From the data obtained for the plasticiser uptake, graphs were constructed and the diffusion coefficient calculated (as previously described for water uptake experiments).

The results of mass uptake and associated data is recorded in table 11. A typical graph is shown in appendix D.

TABLE 11 MASS UPTAKE OF PLASTICISER

Film	Time to M∞	% uptake at equilibrium	Diff. Coefficient m^2s^{-1}
X1	36	6	2.52×10^{-12}
100:20	37.21	17	1.16×10^{-12}
100:40	25	4.5	1.45×10^{-12}
100:50	25	3.75	1.45×10^{-12}
100:60	33.64	1.8	1.3×10^{-12}
100:80	25	0.9	-
100:100	25	1.6	-

As can be seen there is a relationship between plasticiser content and mass uptake of plasticiser by the cured film (table 11). The levels of uptake suggesting an equilibrium concentration of approximately 55%.

This would appear to indicate that at levels of plasticiser above 55-60 parts by weight per 100 parts polymer the matrix is saturated as levels above this have little or no uptake.

It was interesting to note that both X5 and X6 showed plasticiser migration out of the film after standing for long periods.

Thus there appears to be a maximum concentration of plasticiser that can safely be used. Also as the films had all shown a significant mass uptake of water it is not inconceivable that where the sealant is in close contact with glass, plasticiser migration could occur leading to bond weakening. This latter point will be examined during the adhesion strength discussions.

It was interesting to note that the filled system X1 and the unfilled system at 100:20 both had the same final polymer plasticiser ratio. This would suggest that the use of unfilled systems for plasticiser migration is valid.

9 COLD WATER EXTRACTION OF CURING AGENT

As mentioned in section 8 previous workers had found a relationship between mass uptake of water into the film and water solubles in polysulfide sealants. In the earlier work the curing agents had been chromates and dichromates which are themselves largely soluble in water.

In this work however the formulation ingredients are largely insoluble, but as mentioned in the sealant section there is a variable amount of the activating alkali present on the manganese dioxide.

It was considered useful to examine how much water soluble extract was present in the various manganese dioxide powders and to establish what effect the concentration of water solubles had on the diffusion coefficient.

Extractions were carried out on the manganese dioxide powder in cold water.

9.1 EXTRACTION PROCEDURE

An apparatus designed and developed by MRPRA was used to effect the cold water extraction. Other workers such as Khan Kadim(74), and Gick (68) have used this modified soxhlet apparatus in cold solvent extractions. However in this experiment distilled water was used as the solvent.

The manganese dioxide powder was contained within a soxhlet thimble and the extraction carried out over 2 x 8 hour periods. The period was established by a trial test when extraction was continued until constant weight was assured.

9.2 RESULTS OF COLD WATER EXTRACTION

The weight loss of the different manganese dioxides used in the evaluation is shown in table 12. Identification of the products is given using the manufacturers name and code number.

TABLE 12 COLD WATER EXTRACTION DATA

Source of MnO_2	% weight loss
EAGLE PICHER G1065	7.35
SHEPHERDS 54237	8.1
SHEPHERDS 54401	4.5
COOKSONS 1/89	9.44
COOKSONS 2/89	11.06
COOKSONS 3/89	41.32

9.3 COMPARISON OF COLD WATER EXTRACTION RESULTS WITH MASS UPTAKE OF CURED FILMS

By comparing the cold water extraction data (section 9.2) to mass uptake data of the cured films using the manganese dioxide products from various manufacturers it can be seen that whilst there is little correlation of mass uptake with the content of water solubles in the MnO_2, as shown in figure 20, there is some evidence to suggest that the diffusion coefficient of water and time to reach equilibrium are related to the content of water solubles as shown in table 13. The diffusion coefficient is proportional to the water soluble content as shown in figures 21.

Table 13 below sets out the data associated with the water soluble content experiment.

TABLE 13 DIFFUSION DATA OF SEALANT X1 CURED WITH MnO_2 SAMPLES AS USED IN THE COLD WATER EXTRACTION

sample ref (see 10.1)	T(inf) (days)	% equilibrium mass uptake	T(1/2) (days)	calculated D x10^-14 m^2s^{-1}
G1065	225	50	56.25	1.01
54237	210	50	49	1.15
54401	210	60	49	1.15
1/89	49	25	9	6.3
2/89	156	54	36	1.57
3/89	22.6	60	4	14.1

FIGURE 20 MASS UPTAKE V WEIGHT LOSS

based on data from different curatives

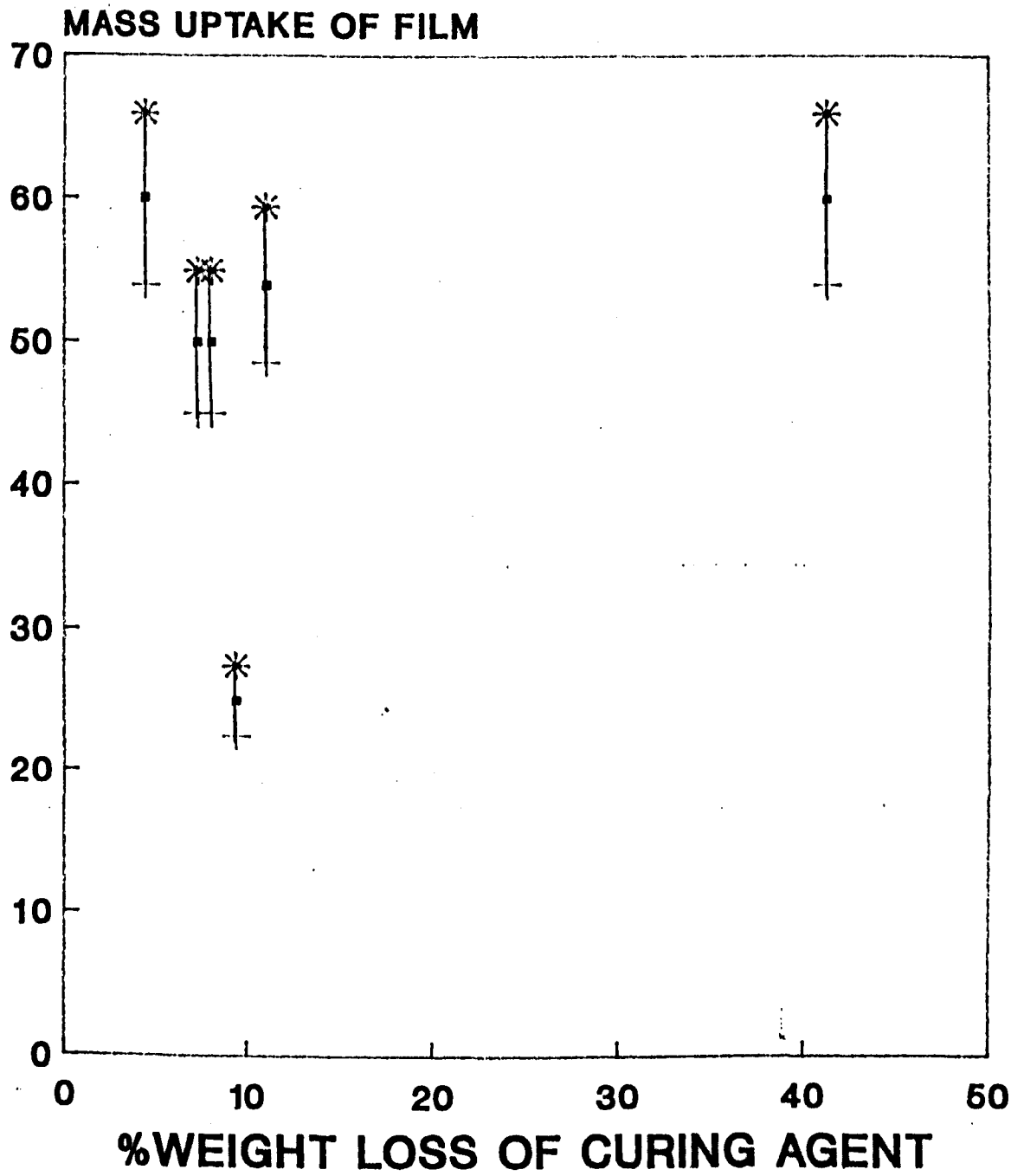
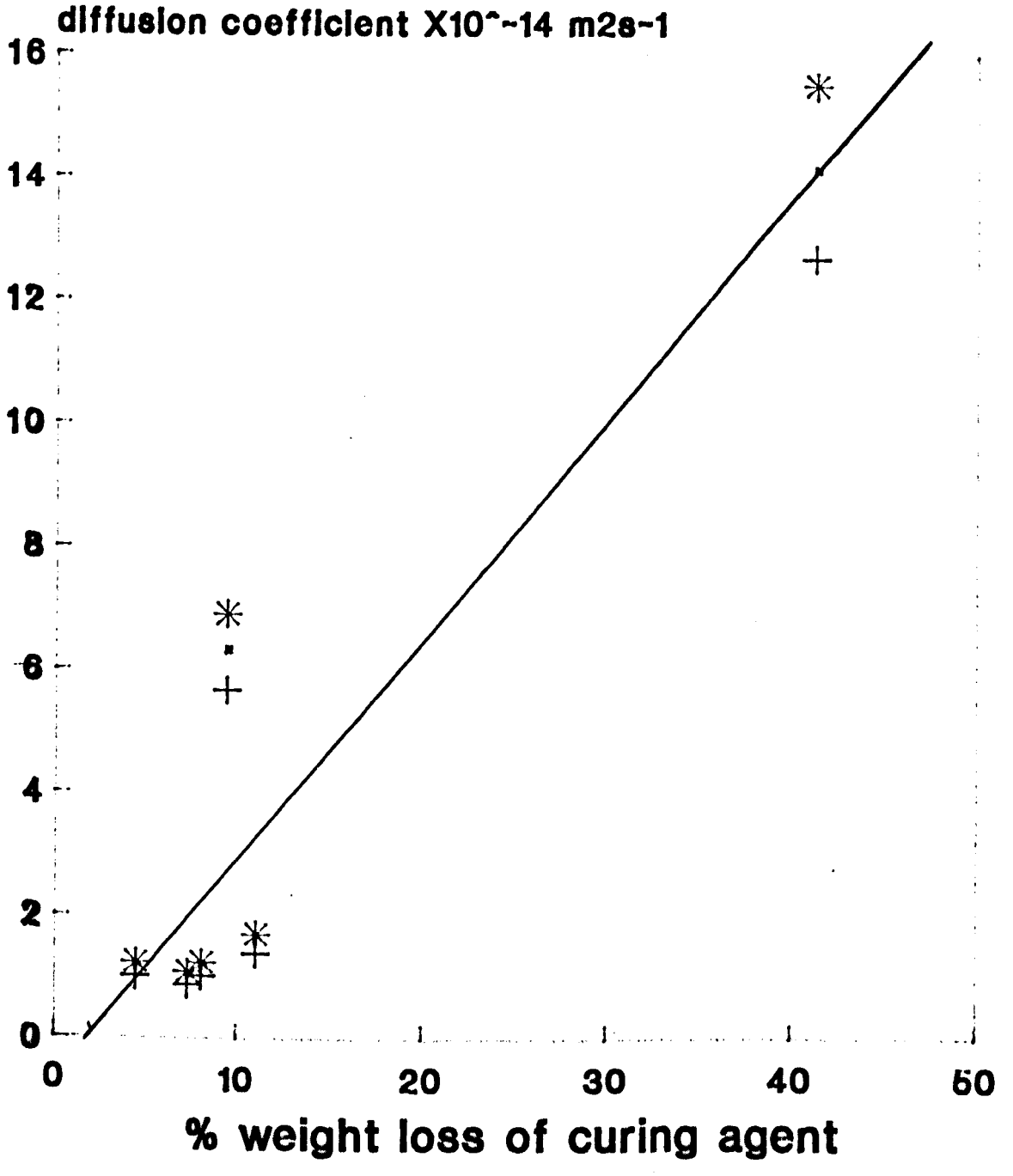


FIGURE 21 WATER DIFFUSION COEFFICIENT V WEIGHT LOSS



10. ADHESION TESTING

10.1 PREPARATION OF GLASS SURFACE AND BOND ASSEMBLY

The glass used in the adhesion experiments was 4 mm. float glass cut to 50 mm. x 50 mm. squares. The glass was cleaned twice with a proprietary glass cleaner which was a water / 2-propanol / ammonia mixture.

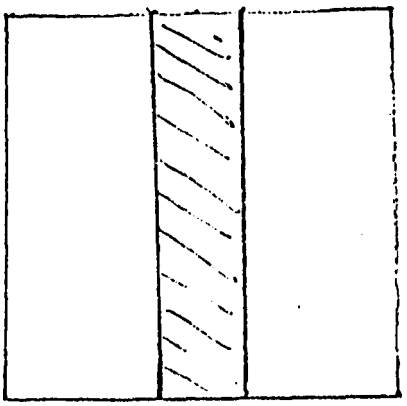
No account was taken of the glass being "sided" in that the floated side would have a greater level of tin present. Instead the surfaces were randomly mixed. Earlier work was not ignored in this approach (75, 76) but thought was given to retaining a practical approach which would relate to insulating glass manufacturers.

The joint was made up as two parallel facing surfaces into which a joint 50 mm.x 12 mm. x 12 mm. could be formed. These are known as H bonds and their preparation is fully described in BS4254 (77).

A typical assembly is shown in plate 4 and detailed in figure 22.

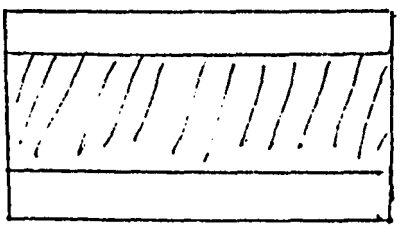
Following assembly the bonds were allowed to cure for 7 days at 23°C and 50% R.H. before the initial bond strength was measured as an average of four test assemblies. The remaining bonds were placed in the

FIGURE 22 ADHESIVE JOINT CONSTRUCTION

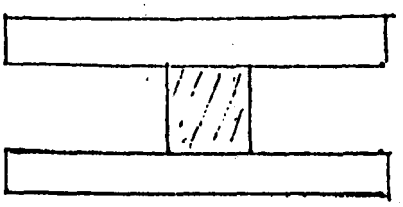


TOP VIEW

SHADED AREA REPRESENTS SEALANT



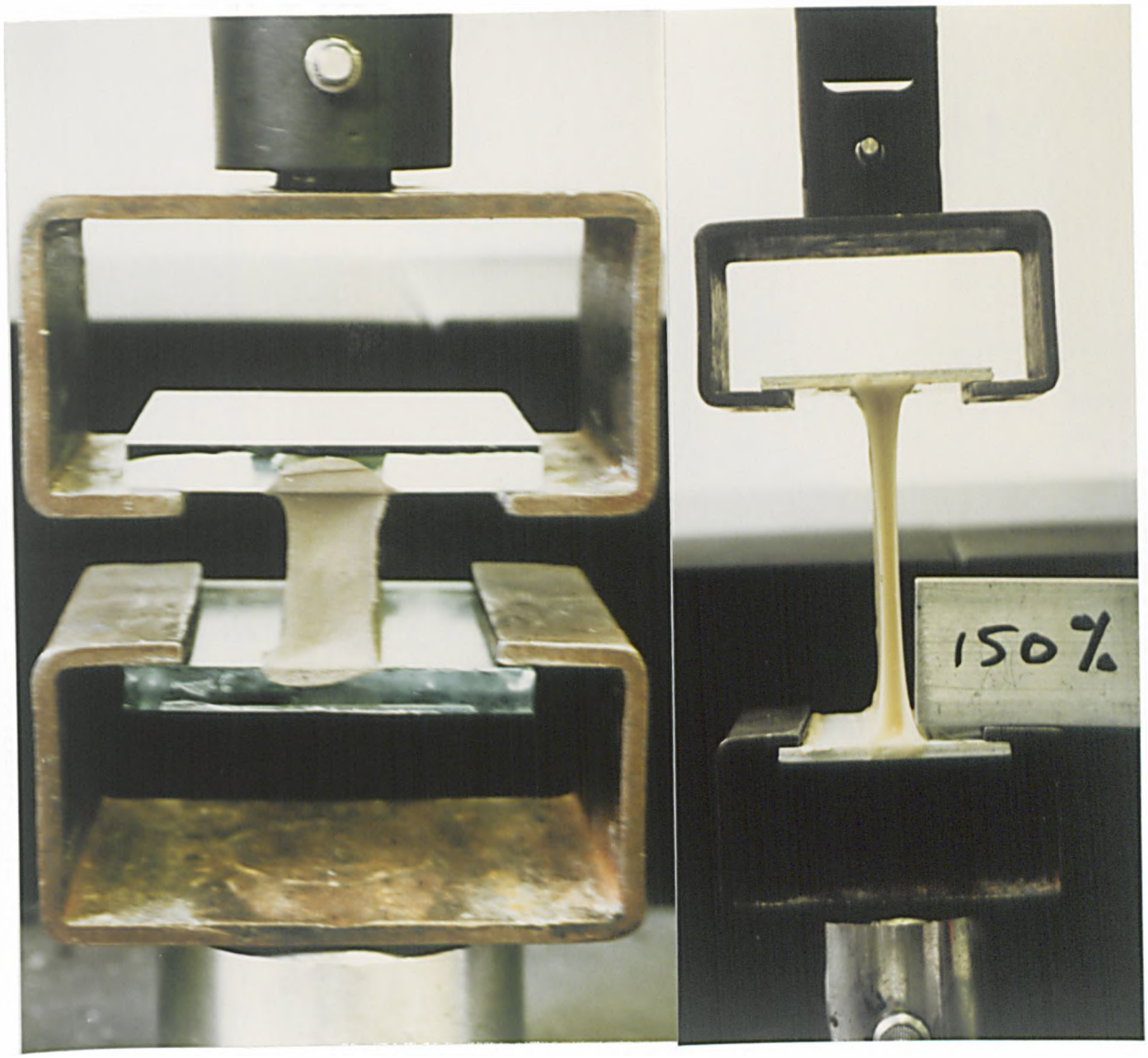
SIDE VIEW



END VIEW

PLATE 4 SHOWING A GLASS-SEALANT-GLASS JOINT HELD IN TENSOMETER GRIPS.

The left side shows the bond before tension is applied,the right picture shows the bond just at the commencement of failure, the tear beginning just above the lower glass plate.



environmental chamber to be tested at regular intervals. Long term testing in wet environments has been used for testing aircraft structures with great success (78,79,80,62).

10.2 METHOD OF TEST

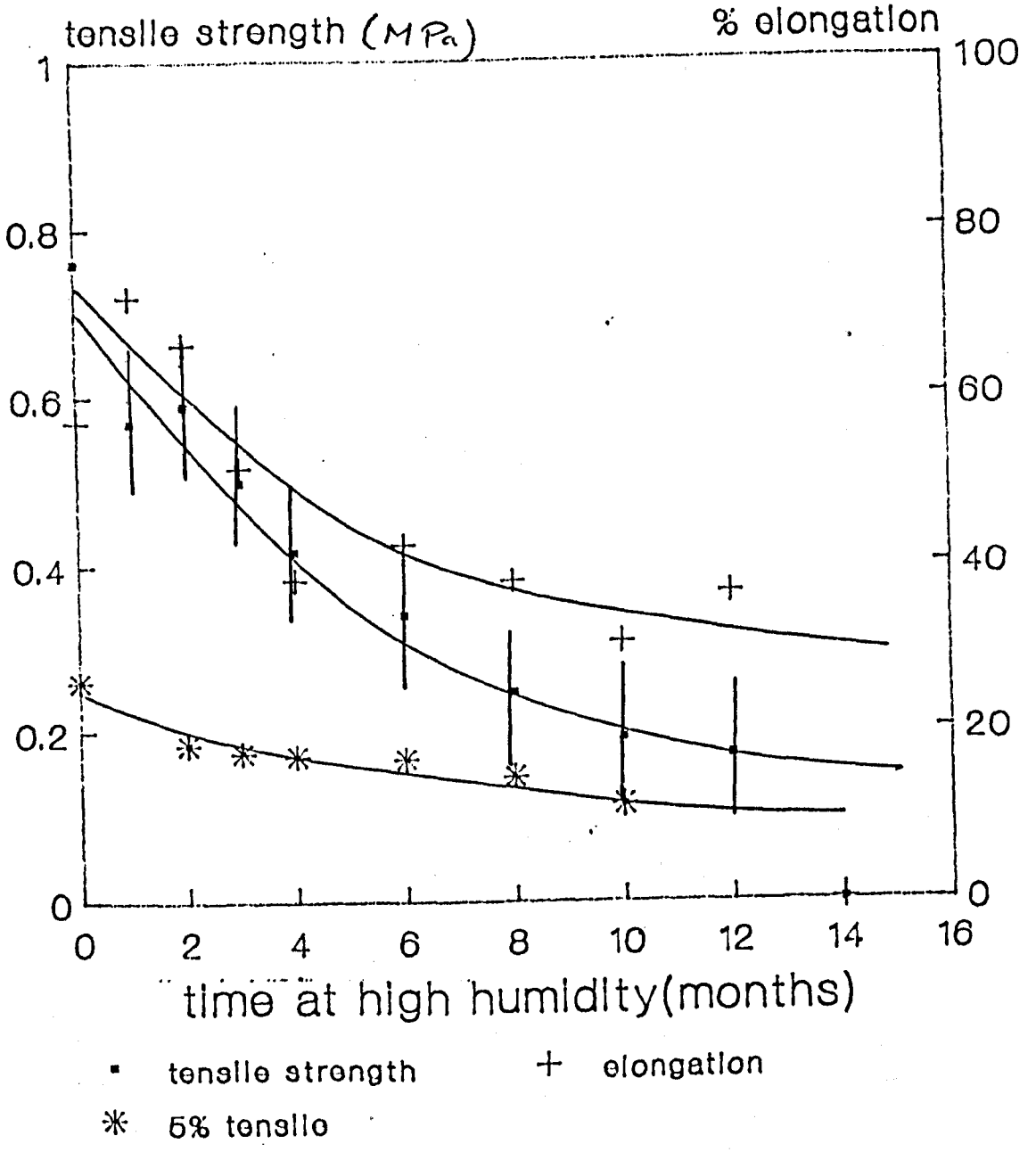
All the joints were tested on an Instron tensile testing machine model No. 1026, in tension. That is the glass surfaces were separated by being held parallel and parted at a separation speed of 6 $mm.min^{-1}$. Separation was continued until failure, either adhesive or cohesive occurred, as depicted in plate 5.

The type of failure together with the extension to break, force at 5% extension and force at break were noted. All test results are an average of four joints and testing was carried out over a fourteen month period. A typical chart of results is shown in figure 23. A typical stress-strain plot is shown in appendix E. The bonds were photographed after test. A record of the bond test results appears in Appendix F.

10.3 ADHESION STRENGTH AFTER DRYING

The mass uptake experiments had preceeded the adhesion experiments and

FIGURE 23 ADHESION TEST RESULTS SHOWING THE EFFECT OF AGEING ON ADHESION USING X1



The figure shows tensile adhesion strength,adhesion strength at 5% extension and elongation to break all as a function of ageing time. Note only the error bars on the tensile adhesion strength are shown for clarity.

PLATE 5 Photograph showing the different types of bond failure. Top shows 100% cohesive failure whilst the bottom photograph shows mixed failure. adhesive failure.

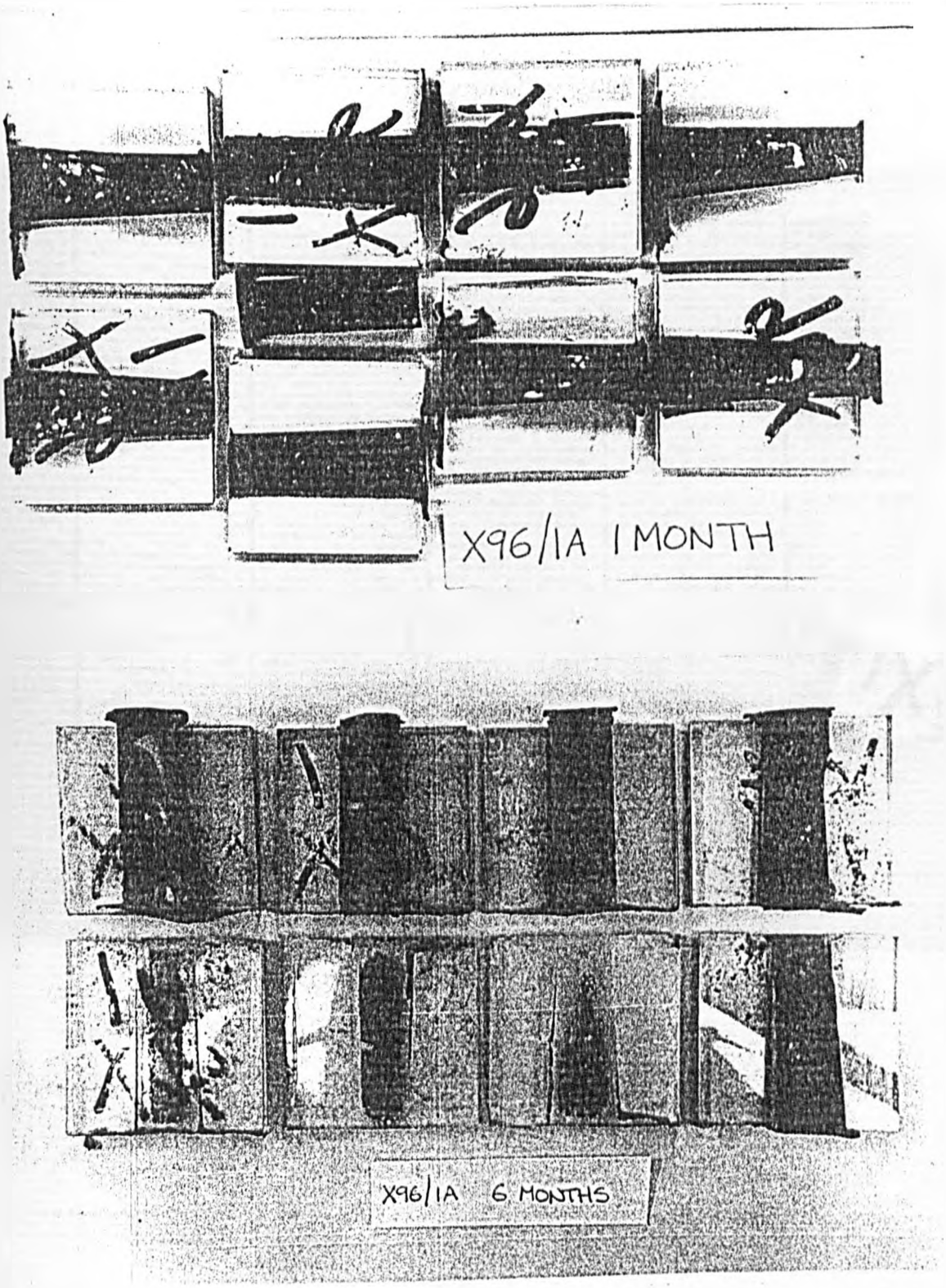
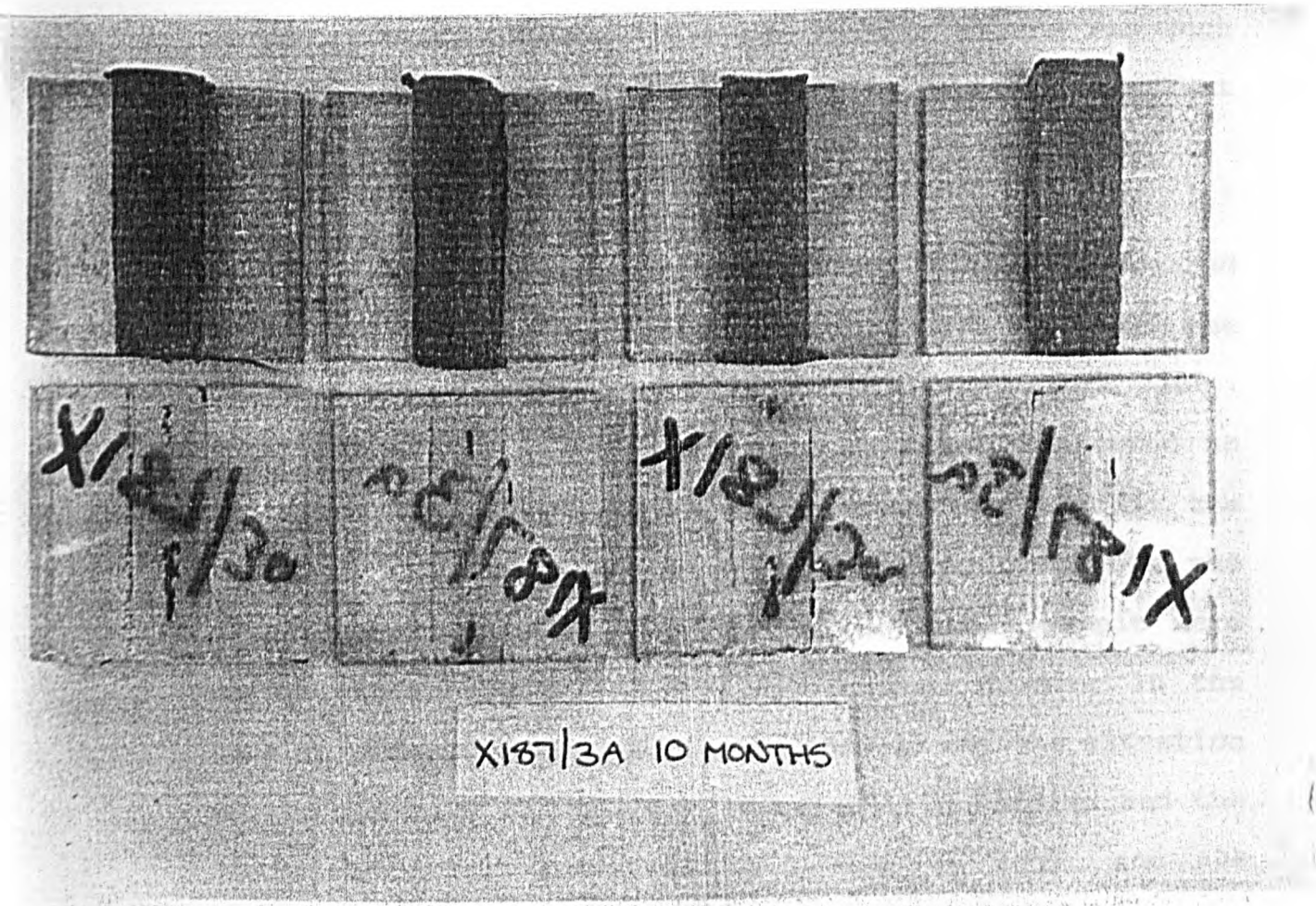


PLATE 5A Photograph showing total adhesion failure.



two particular points were noted. Firstly, as the period of time in the ageing chamber increased, the apparent strength of the adhesive decreased. The D.M.T.A. results showed little ageing effect and the Youngs modulus of the initial sample and that of the aged sample were very similar.

Secondly it was observed that the rate of drying was such that it took 28 days for the films to approach constant weight.

As the mass uptake and subsequent drying appeared reversible it was necessary to establish whether the adhesion loss and loss in tensile adhesion strength was also reversible. The initial DMTA work had indicated no loss in physical properties and it could be that in the case of the DMTA the rate of heating together with the temperatures achieved on a relatively small sample were sufficient to cause significant drying. However in the case of the adhesion experiments this is not the situation as the quantity of sealant is relatively massive and the bonds are only subjected to 1 hour at 25°C and 50% relative humidity (R.H.) before being tested.

It was decided therefore to examine bonds, which having being taken to the point of significant adhesion failure (1 year in the ageing chamber) as adjudged from 10.2, were then allowed to dry at 25°C and 50% R.H. for up to 1 year. The bonds were tested at regular intervals to establish

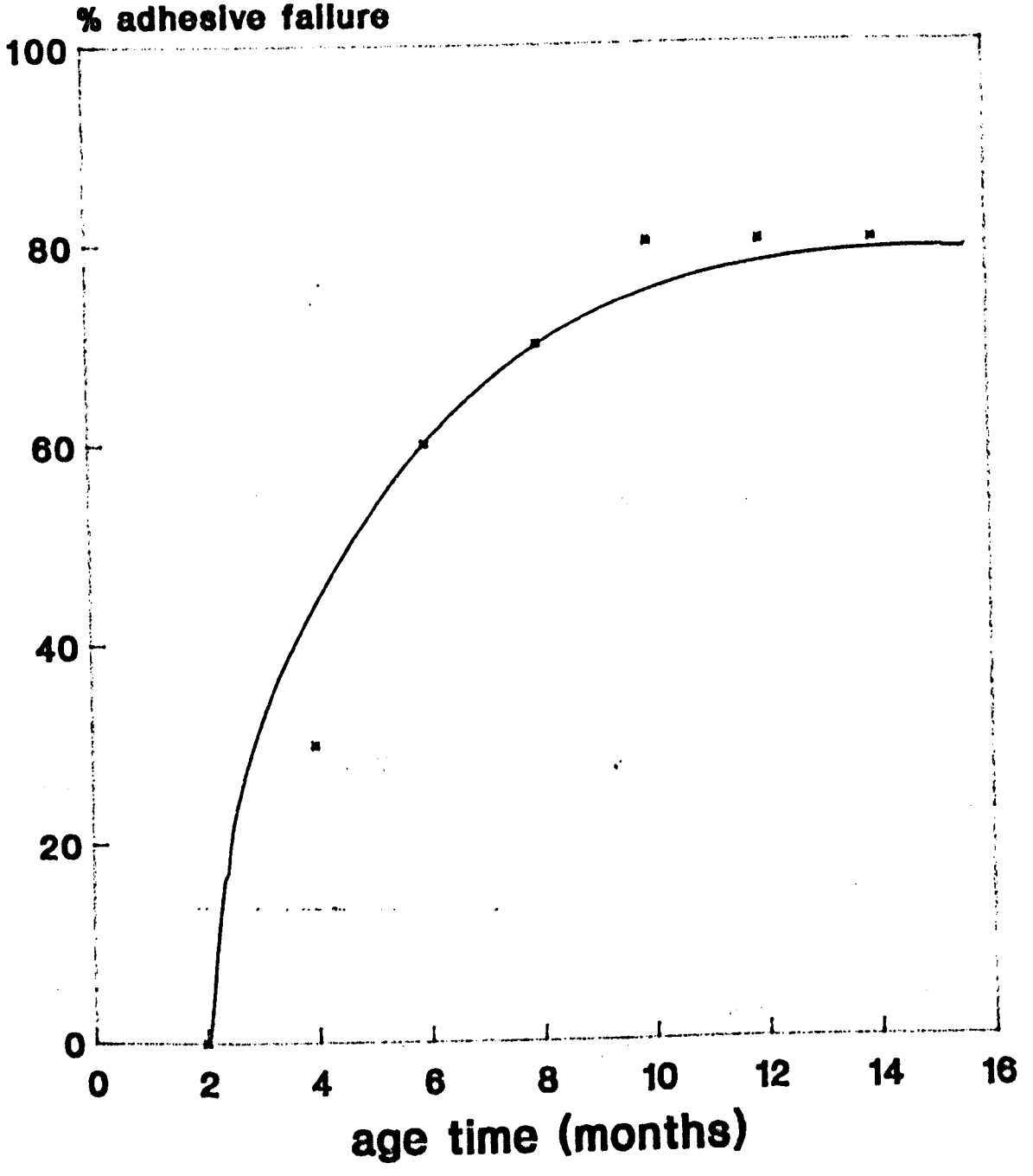
whether the trend to failure is totally reversible or not, and whether the tensile strength of the sealant is restored. A number of bonds were made and subject to the ageing conditions as defined earlier. The bonds were not disturbed during the ageing period of 1 year. At the end of the ageing period all the bonds were removed from the environmental chamber and four bonds were tested within 1 hour at 23°C and 50% relative humidity.

The next bonds were tested after 48 hours drying and thereafter bonds were tested at variable intervals which was dependent on the results obtained. That is, where little recovery was noted the period between tests was extended in order to obtain as much information as possible with the samples available. The results are discussed in section 10.5 and shown in figure 28.

10.4 ADHESION TEST RESULTS

The adhesive bonds were tested at monthly intervals initially followed thereafter by bimonthly intervals. The plots shown in figure 24 of adhesion strength against time shows tensile strength at break, elongation to break and tensile stress at 5% extension. This graph is typical of all the sealants tested with the exception of formulations X5 and X6 (see tables 3a and 3b section 5.1.1) which showed almost immediate adhesion failure.

FIGURE 24 TYPICAL CHART OF ADHESION FAILURE AFTER AGEING AT 60°c. AND 100% R,H,



Some of the systems exhibited increasing adhesion failure with time in the environmental chamber, the failure spreading from the edge of the bond. The increasing area of bond loss was assessed visually and the average area of bond loss was plotted in bar chart form against time. Figure 25 shows a typical plot of these results. Further plots of these are shown in appendix G. It was noted that the initial tensile adhesion strength decreased with increasing plasticiser content. This is in line with commonly held views on polysulfide based seqalants.

The energy of break was calculated from the areas under the modulus curves and the relationship between this value and the decay in adhesion can then be plotted. A typical graph is shown in figure 26.

It was noted following the photographing of the joints that a discoloured area appeared at the interface. This coloured area was a brown discolouration which deepened where adhesion failure occurred. Attempts were made to measure the rate of growth of this area against loss in bond strength and correlate this to the diffusion coefficient. The rate of growth of the discoloured area was measured from the photograph using a ruler and the results scaled up to take into account the size of the photographed bond to actual size. The width of the discoloured area as measured is referred to as boundary length. Figure 27 shows a typical plot of the change in

FIGURE 25 ADHESION BREAKDOWN

showing that as tensile adhesion strength reduces with ageing time the failure area increases of X1.

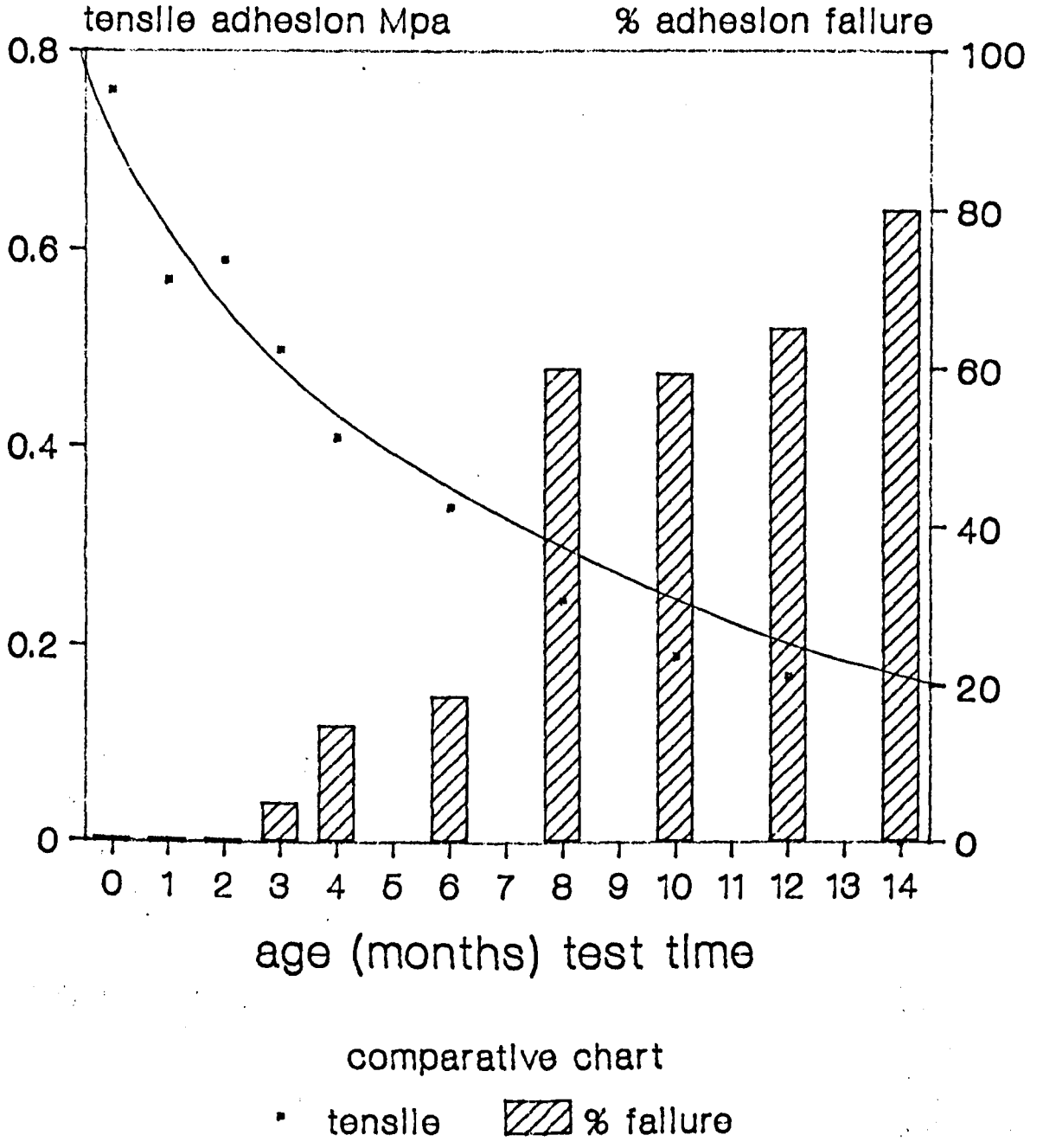


FIGURE 26 ENERGY TO FAILURE

The energy is represented as the area under the curve, and is equal to the sum of the cohesive and adhesive strength. The points show the mean +/- standard deviation

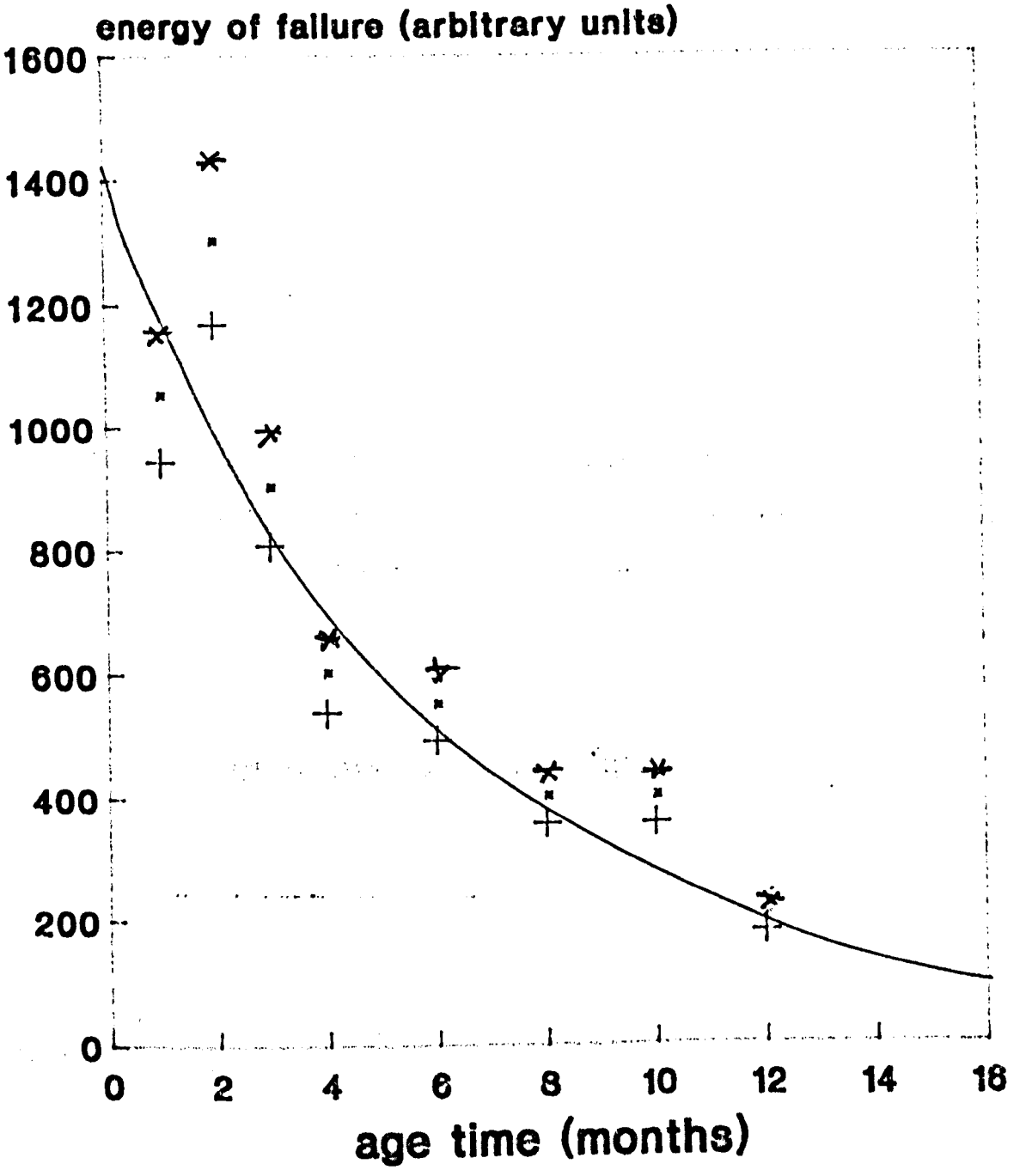
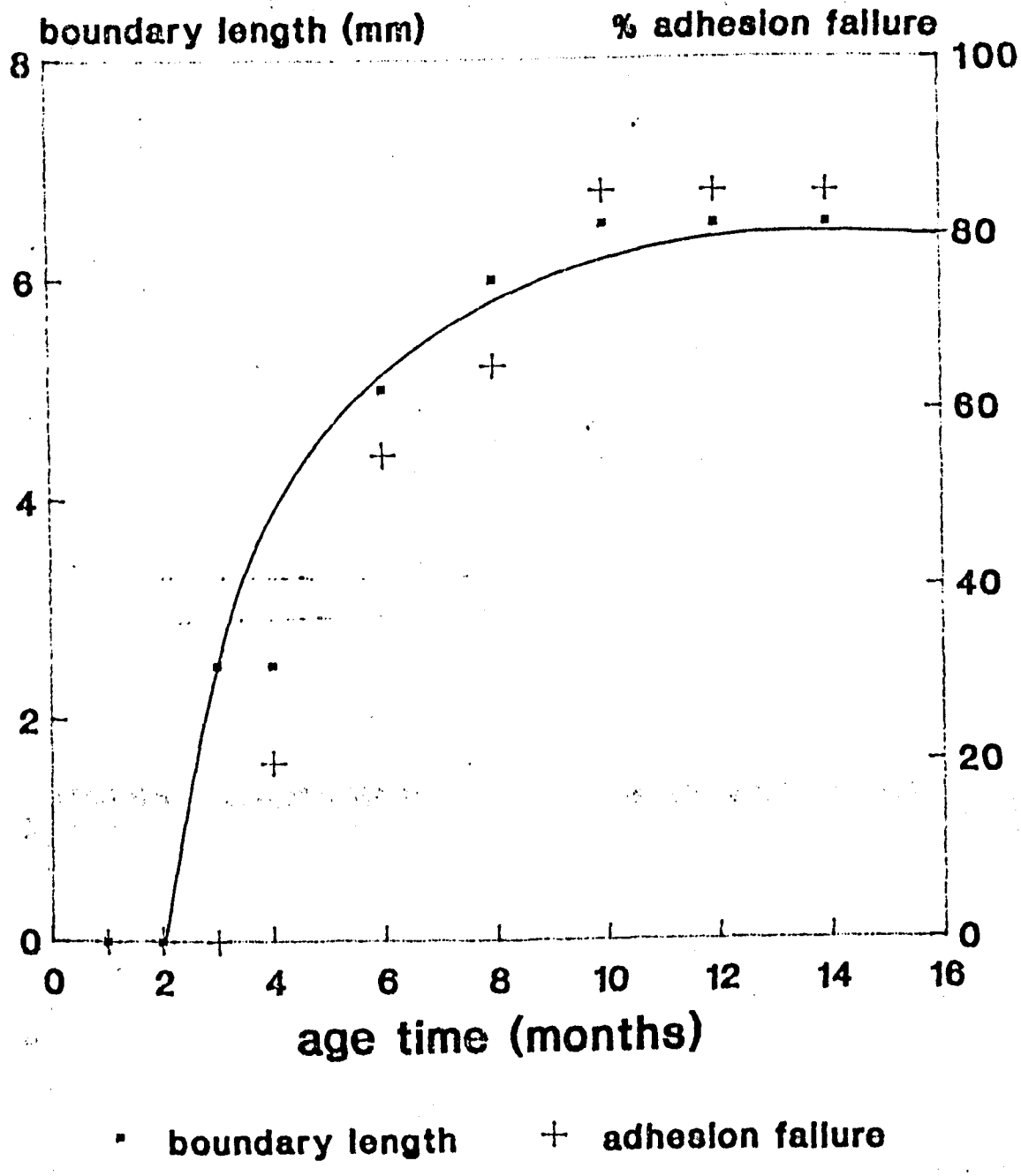


FIGURE 27 BOUNDARY LENGTH V AGEING TIME

based on formulation X1, the visible boundary precedes the adhesion fail line but follows a similar pattern.



boundary length against ageing time. Further plots can be seen in appendix H.It was seen for all sealants that the discoloured area preceded adhesion failure, and the area of joint interface between the boundary layer and the external face of the joint was the area of adhesion failure.

It was speculated that the growth in the discoloured area was due to water diffusion. During dicussions with workers at Toray-Thiokol, it was disclosed that NMR studies had led to the conclusion that the dicolouration was due to formation of high sulfur containing species. This could be a possibility as due to the elevated temperature and high concentration of water any residual manganese dioxide curing agent could be induced to form oxidative radicals. It should be noted from the photographs that the centre of the bond was the last area to lose adhesion.

It was noted that a number of workers had shown bond loss related to exposure conditions. Such workers include Kenig (86), Bishop (87) and Gaur (88). Other workers had examined the possibility of a critical relative humidity in relation to bond strength degradation. Such work includes that of Kinloch (89) and Lefebvre (90).

10.5 ADHESION STRENGTH ON RECOVERY

After one years ageing in the environmental cabinet the

joints were all removed simultaneously. One set (four bonds) from each formulation set were tested within two hours. The remaining bonds were placed on a tray and allowed to age in laboratory air at 23 °C and 50% R.H. An air conditioned laboratory was available for this purpose controlled to 23+/-2°C and 50%R.H. The intervals of drying between tests became increasingly longer as the test progressed, the time periods are given in table 14.

Although the joints tested immediately were still wet and later bonds tested later were apparently dry there was little change in strength at failure over the first 6 months period. Also some appeared to weaken slightly as they dried out. This tended to demonstrate that any weakening of the joint was irreversible. Joints tested after 1 years drying showed an increase in bond strength and most had recovered to at least the initial value of the wet bonds.

TABLE 14 DRYING PERIOD FOR ADHESION STRENGTH BUILD UP TEST

immediate
2 days
7 days
14 days
29 days
41 days
92 days
213 days
365 days

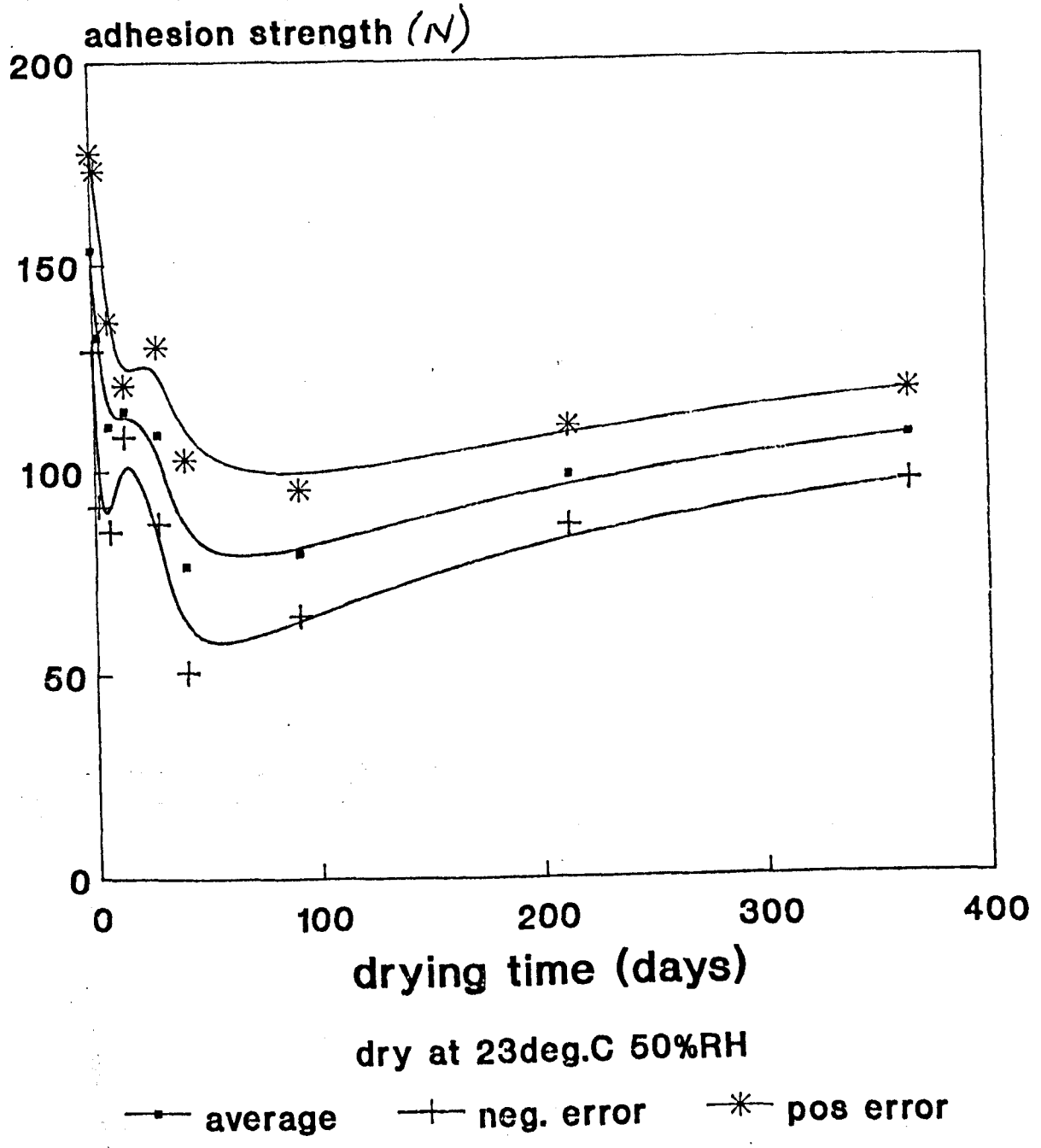
The type of failure remained the same. In all cases the joints had debonded from the outside towards the centre. In most cases the joint remained fractionally intact in the centre, it was this area that failed cohesively on testing and showed the increase in bond strength. There was no healing of the area where weakening or failure had occurred.

An average of the tensile adhesion strength of the four bonds tested after each drying interval was plotted against drying time. A typical curve is shown in figure 28. The initial fall in adhesion srength is possibly due to the removal of water which has a plasticising effect on the sealant. All the systems showed a similar behaviour with slight recovery in adhesion strength being observed between 50 days and one year. Further plots of these can be seen in appendix I.

This indicates that the adhesion loss is irreversible and the boundary layer at the glass-sealant interface is permanently damaged.

From the adhesion tests carried out, there were two distinct modes of adhesion failure observed. Firstly there was the extremely rapid onset of failure caused by plasticiser migration as discussed in section 10.4. Secondly there was what appeared to be a diffused water induced failure as discussed in section 10.5 which was

FIGURE 28 ADHESION STRENGTH RECOVERY PLOTTED AS BOND STRENGTH V DRYING TIME



manifested by an apparent weak sealant/glass boundary layer as discussed in section 11.

10.6 RELATIONSHIPS BETWEEN ADHESION AND DIFFUSION

Of the various mechanisms of adhesion failure, three appear to be the most likely to play a major role in the sealant/glass joints used here. These are diffusion of plasticiser to the interface, where it constitutes a weak boundary layer, and in severe cases displaces the sealant. This is referred to as type 1.

Type 2 is the diffusion of water to the interface where it could displace the sealant , and type 3 is defined as being hydrolysis of the sealant.

The possibility exists of a combination of types 1 and 2 whereby the diffused water displaces the plasticiser to the interface, thus causing weakening and eventual adhesion failure.

The plasticiser migration theory for type 1 mechanism of failure was confirmed by swabbing the glass surface, from an assembly of sealant X5, with an ether solvent and checking any material removed by Infra-red spectrophotometry (I.R.) The IR traces confirmed residual plasticiser on the glass, the identification being carried

out in transmission on a Perkin Elmer 781 spectrophotometer. In the worst case a visible layer of plasticiser had formed on the glass-polysulfide interface during the initial 7 days curing period. Figure 29 shows the I.R.trace from the interface, whilst figure 30 shows a trace of the pure plasticiser,santiciser 278, used in this work.

It should be noted that the I.R. of a polysulfide is very distinctive and no indication of polysulfide was evident on the test traces.

Because the failures on X5 and X6, the two systems with the highest plasticiser content, were so catastrophic it was not possible to determine whether the plasticiser build up on the surface increased with time. An observation was made on the films used for DMTA and diffusion as they were stored in the laboratory after testing was complete. It was noted on some films that there was plasticiser on the surface, the increase could not however be quantified.

Analysis of adhesion failure was shown by X.P.S. analysis to be a cohesive failure whereby only very little sealant was left on the glass surface. The technique is described in section 11. The presence of significant quantities of sulfur on the glass confirmed this view as the only likely source of sulfur in the system is from the sealant. It is this barely visible layer that is referred to as a weak

boundary layer.

The rate of increase of the visible boundary layer observed within the joints matched well with the loss in bond area. It can therefore be concluded that the visual colour change coincides with the area of weakened interface of the glass/sealant joint.

Details of the growth of the boundary are given for joints using X1 in table 15. The boundary had reached the centre of the bond after 6 months. The rate of weakening can be compared with the calculated water distribution within the joints based on the measured diffusion coefficient.

The rate of boundary layer increase should relate to the concentration of water in the bond by the equation

$$C = \frac{Dt}{l^2}$$

where C = water concentration

D = diffusion coefficient

t = time in seconds

l = distance of visible boundary from edge of bond

Using formulation X1 as an example this gives the results shown in both table 15 and in figure 31.

TABLE 15 CALCULATED WATER CONCENTRATION AT THE EDGE OF THE BOUNDARY

age period months	boundary from edge of bond (mm)	calculated concentration (relative (C/C_1))
2	0.5	2.32×10^{-3}
3	2	3.48×10^{-3}
4	3.5	4.64×10^{-3}
5	4	5.80×10^{-3}
6	5	6.95×10^{-3}

It can be shown that complete saturation is not necessary for adhesion failure to take place. This can be demonstrated by calculating the time to saturation using the diffusion coefficients from the film test results as shown in table 11 (page 81). This gives a saturated time to failure of approximately 3 times that actually observed,see figure 32. It can also be seen that the concentration of water adjacent to the failure line increases with time. It is possible therefore that after initial failure the bond is weakened by water passing between the glass and sealant rather than diffusing through the sealant.

FIGURE 29 INFRA RED SPECTRUM OF SUBSTANCE SWABBED FROM GLASS SURFACE OF BOND X1

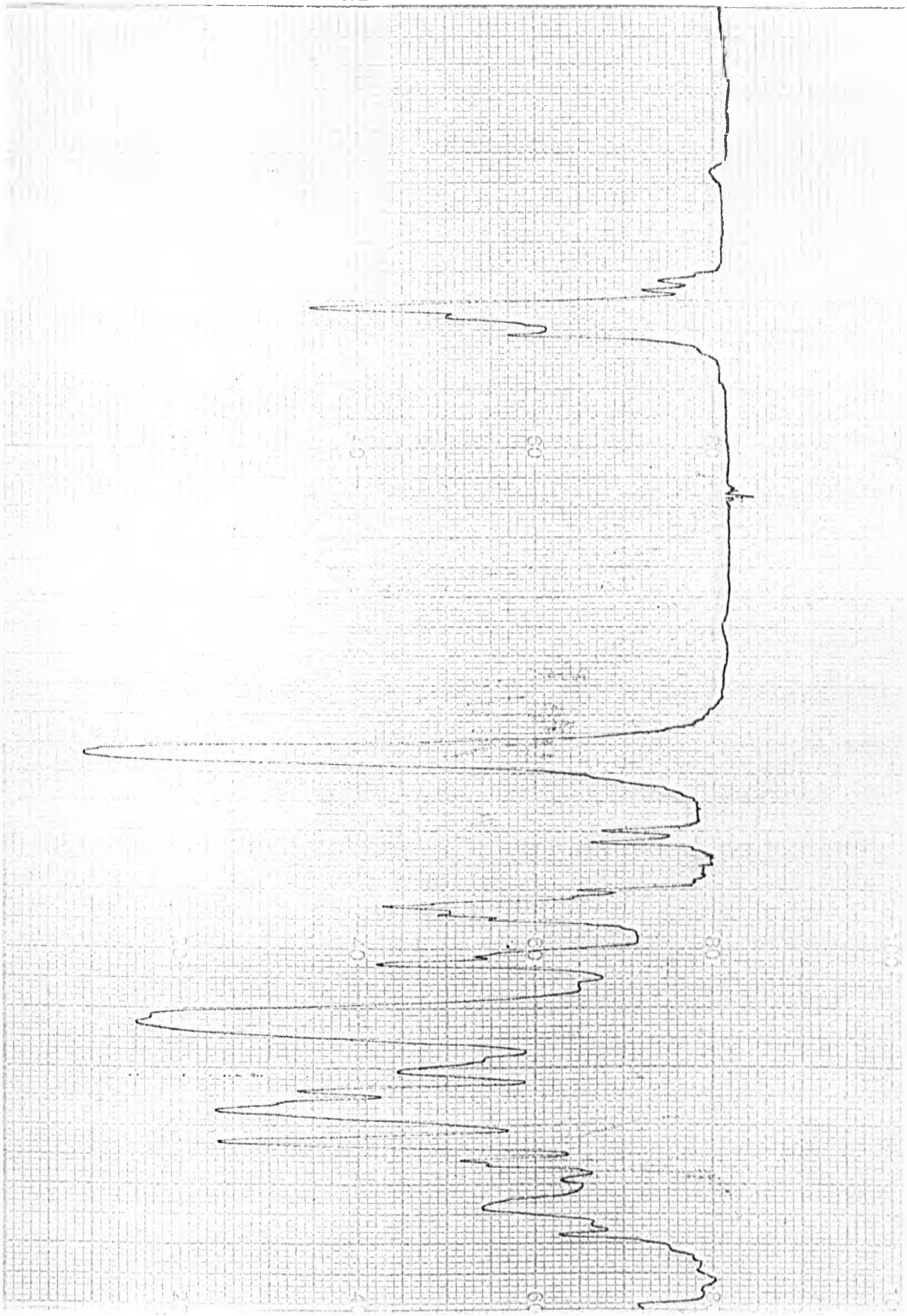
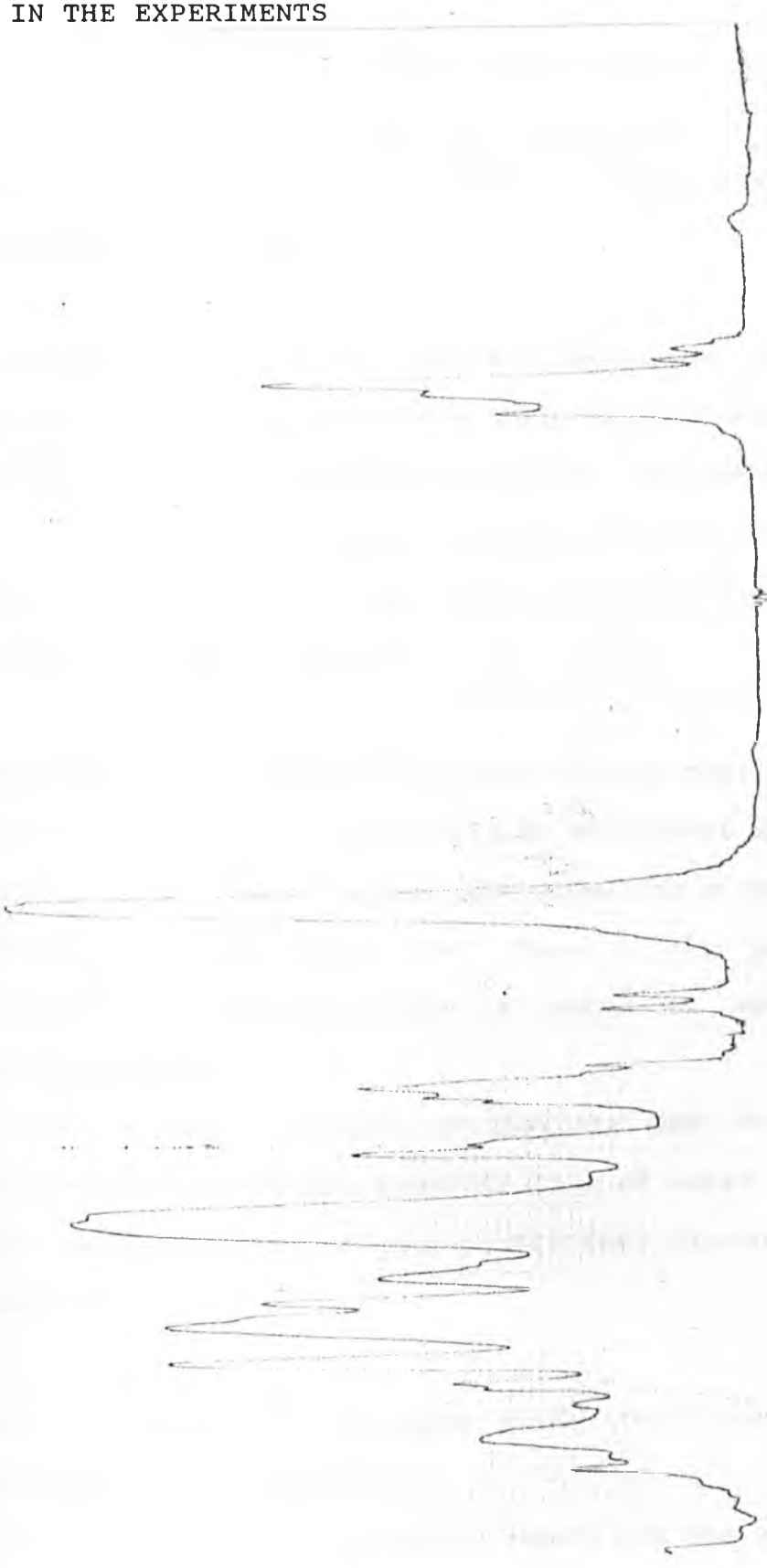


FIGURE 30 INFRA RED SPECTRUM OF PHTHALATE ESTER PLASTICISER USED IN THE EXPERIMENTS



10.7 ANALYSIS OF WATER IN THE BOND

If the rate of travel of water from the edge of the bonds to the boundary is related to diffusion, it should be possible to compare the reduction in strength to the rate of diffusion of water.

The sealant is a block of material measuring 12mm.X 50mm. sandwiched between glass. Water will diffuse into both the long and the short faces of the block, but because of the short diffusion path, water uptake will be dominated by diffusion into the long face. Diffusion into the short face has therefore been ignored.

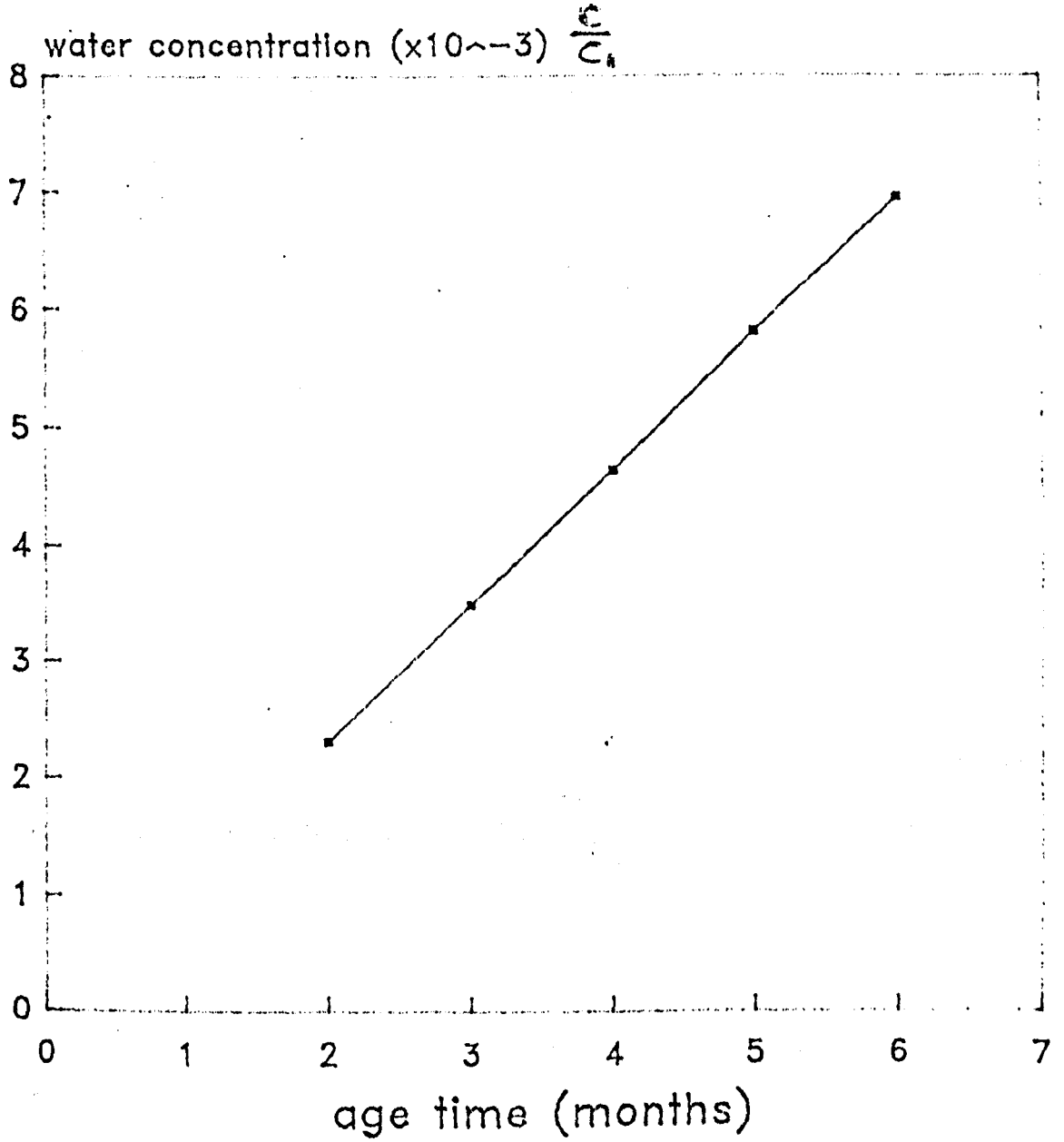
Examination of the bond photographs showed that the time to reach 50% adhesion failure could be estimated as could the boundary layer. These values were used for t and l in the equation given on page 109. Thus it is possible to calculate the concentration of water at the boundary failure interface.

The results shown in figure 32 indicate that the nature of the relationship between concentration of water required to induce adhesion failure and plasticiser concentration is uncertain.

Figure 33 shows an enlarged plot (omitting X1) which reinforces the argument.

Plate 6 shows a set of adhesion bonds and the increase of

FIGURE 31 CONCENTRATION OF WATER AT VISIBLE BOUNDARY LAYER WITH AGE TIME



adhesion failure against time.

It would therefore appear that the progression of bond loss requires increasing concentrations of water with decreasing plasticiser effective, but this may be a balance of properties between adhesion and cohesion as the body of the sealant is weakened in the presence of water. The latter factor is indicated by the almost linear loss in bond strength with time as shown in figure 25.

From the analysis of the results it can be seen that the increase in water content controoled by diffusion causes a loss in tensile adhesion strengthat 5% extension. This however does not indicate a potential for adhesion failure which is predicted to be caused by plasticiser increase at the interface (see section 11 page 120). The loss in bond strength compared to the concentration of water is shown in figure 34.

FIGURE 32 CONCENTRATION OF WATER AT 50%FAILURE PLOTTED AGAINST POLYMER/PLASTICISER RATIO

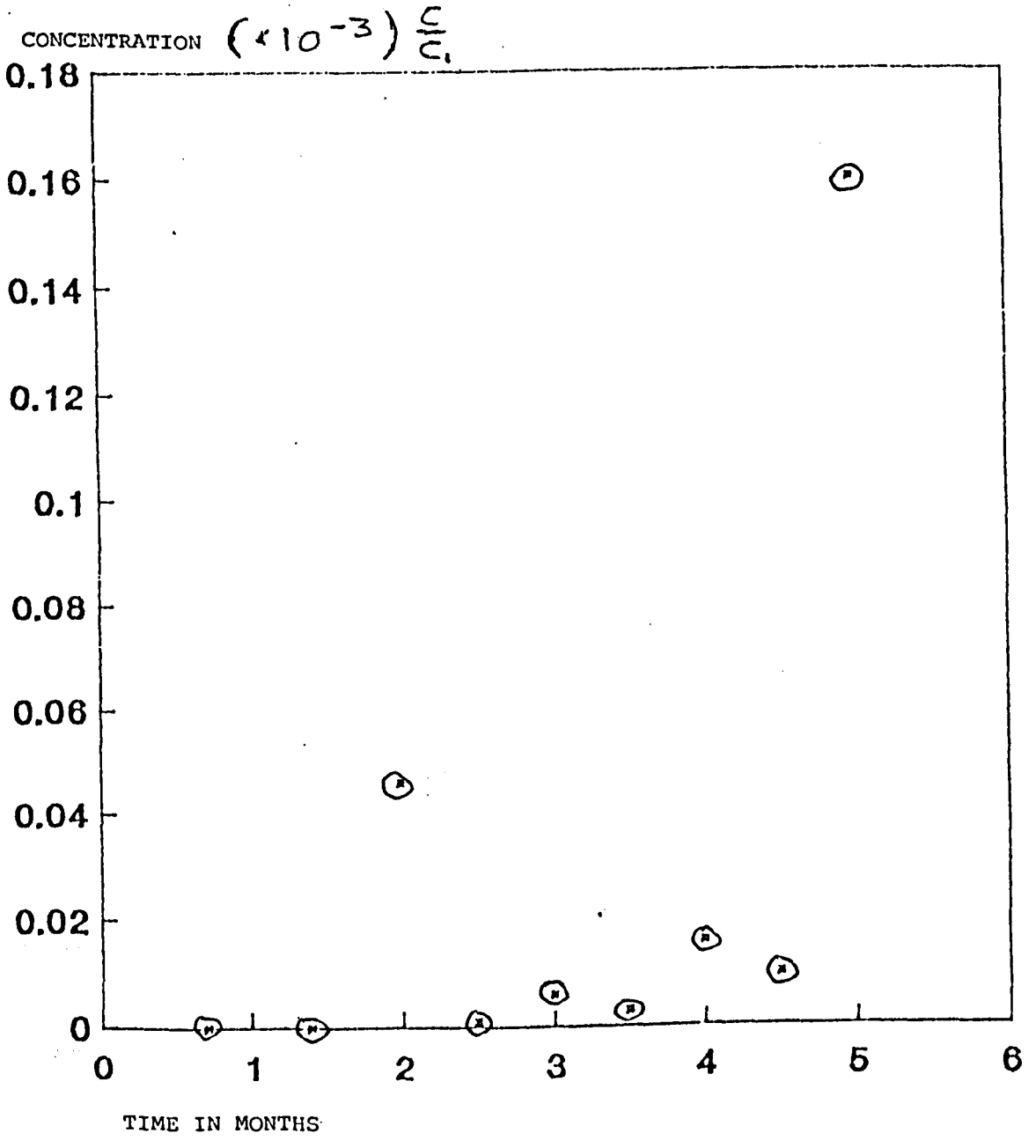


FIGURE 33 ENLARGED PLOT OF FIGURE 32

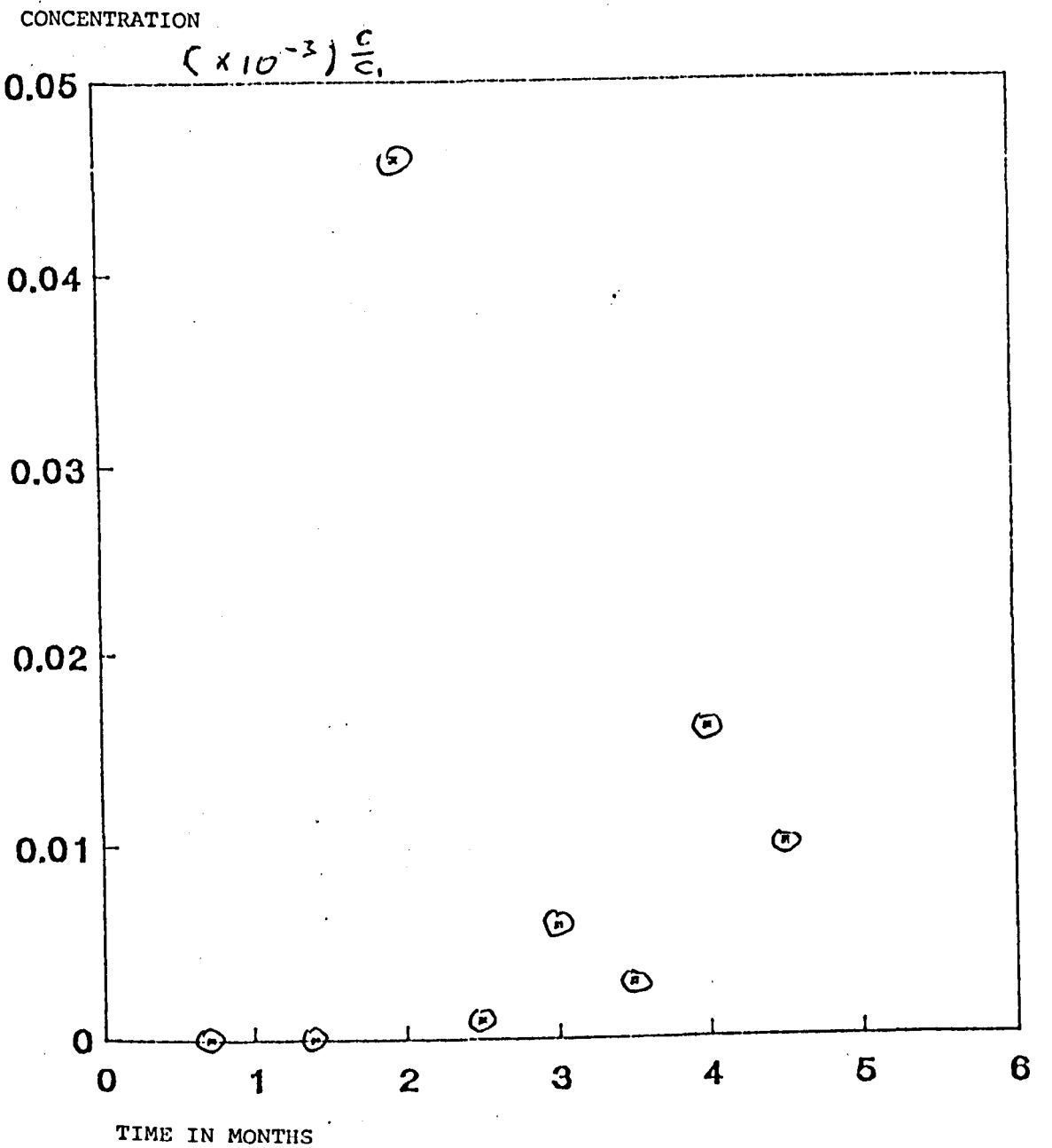


FIGURE 34 PLOT OF WATER CONCENTRATION IN JOINT USING X2

for comparison with plate 6

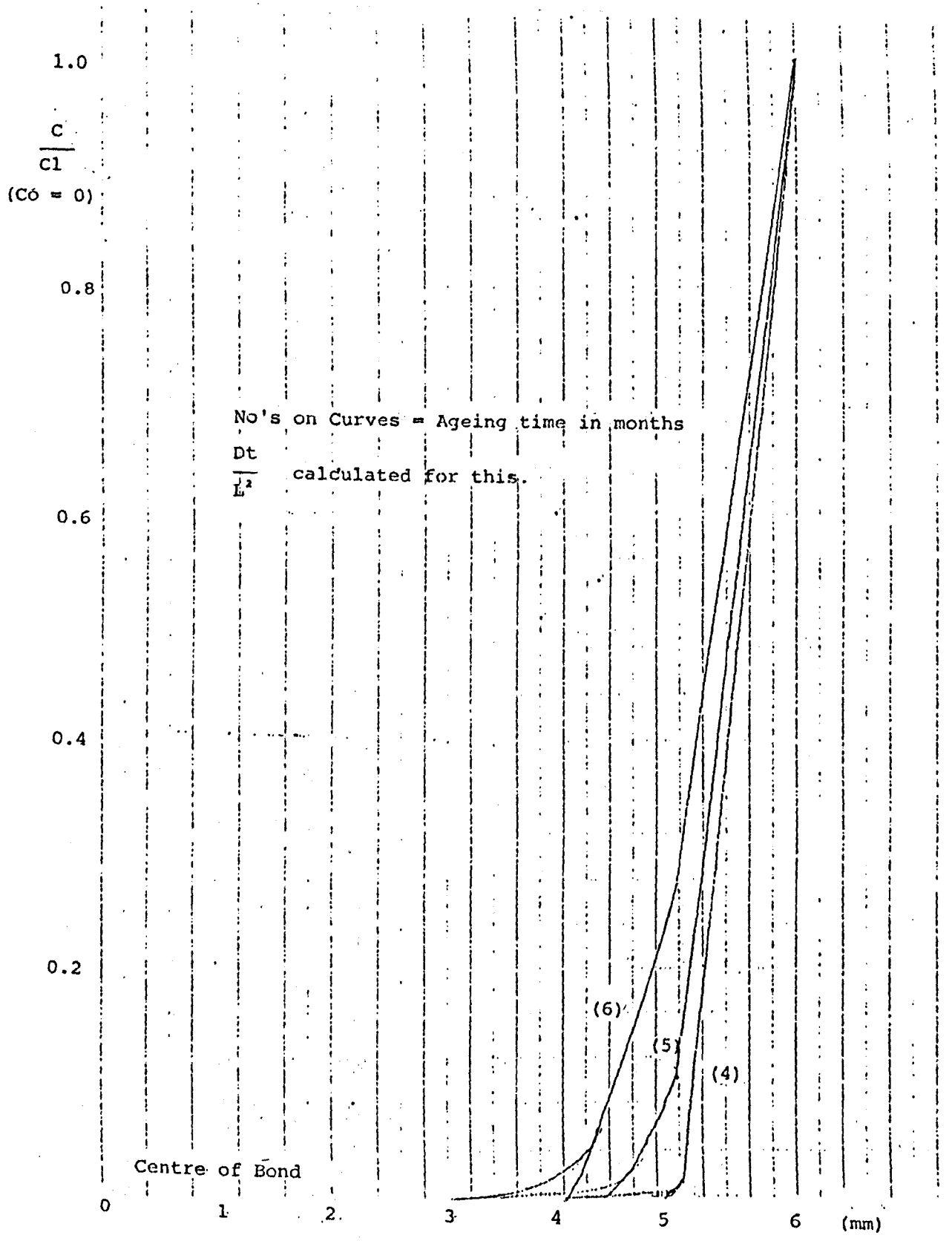
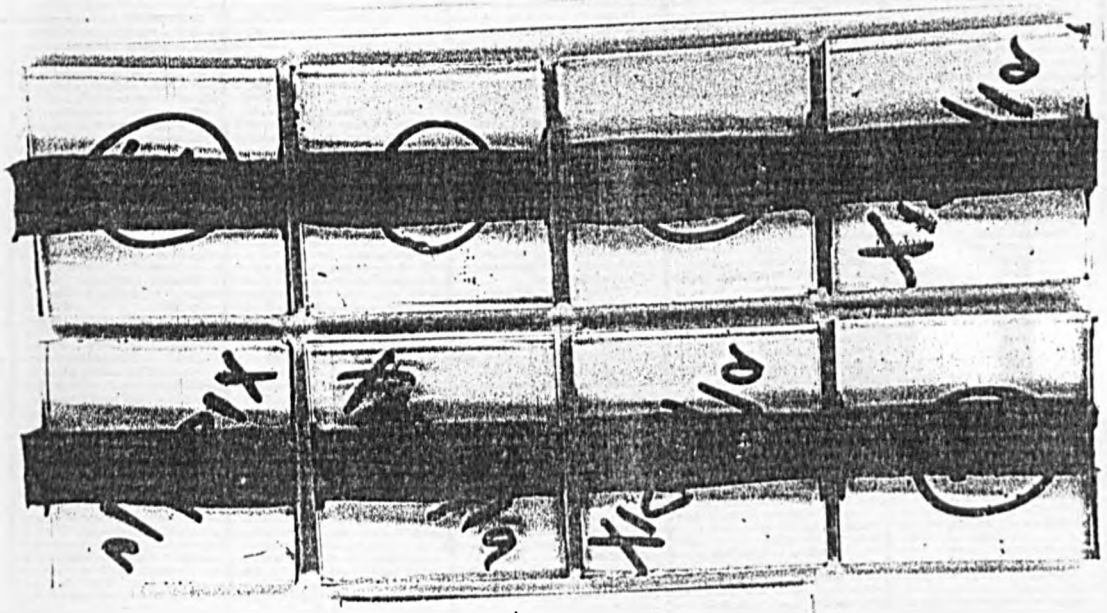
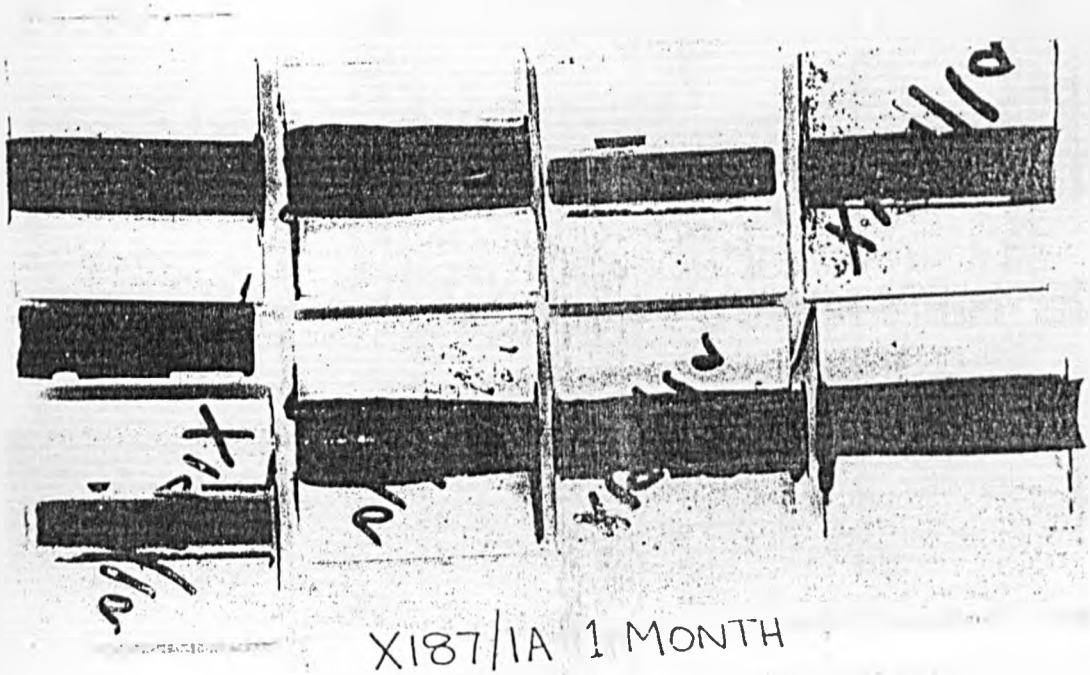
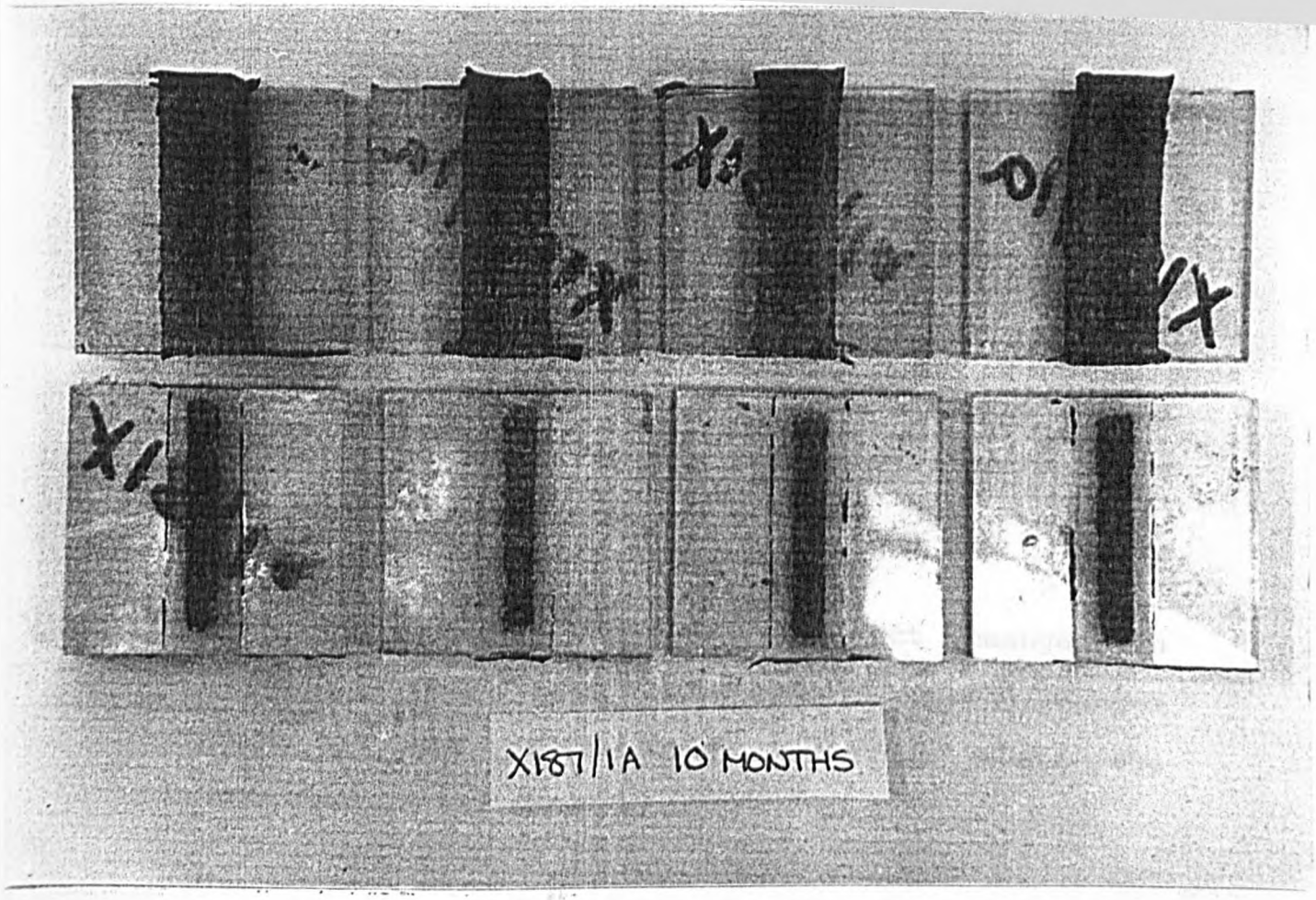


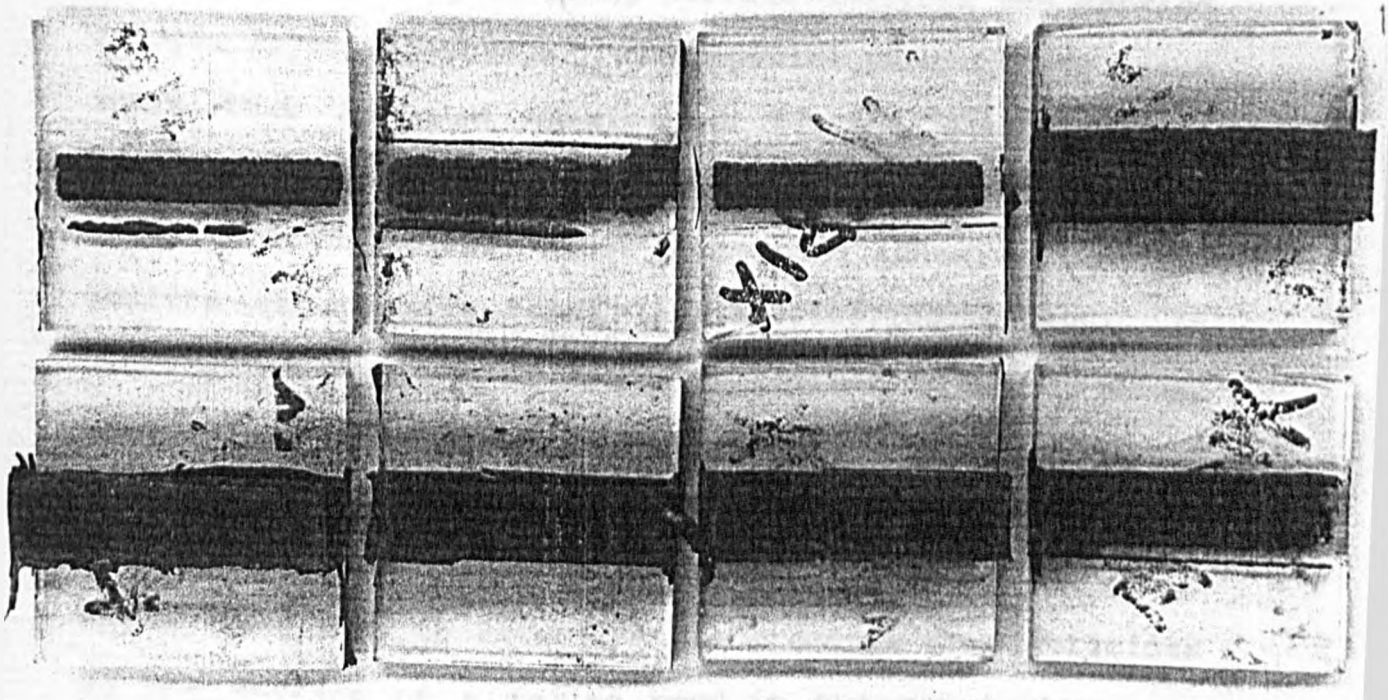
PLATE 6 SHOWING CHANGE FROM COHESIVE TO PARTIAL ADHESIVE FAILURE AGAINST AGEING TIME

for formulation X2









X187/1A 4 MONTHS

11. SURFACE ANALYSIS

It was noted in the adhesion tests that as ageing progressed the mode of failure apparently changed from cohesive to adhesive for all the systems to a greater or lesser degree. This change is represented diagrammatically in figure 25. It was felt appropriate to examine these changes by surface analysis.

The use of surface analysis to detect changes in concentrations of elements can be used to examine changes occurring at the glass-sealant interface where the adhesion failure has occurred.

A literature survey covering surface analysis was carried out (91,92,93,94,95,96,97) with special reference to those works that included examination of the glass surface (98,99,100). A number of papers on surface analysis were referred to especially those concerning adhesives and the failure of adhesive bonds (101,102,103,104,105,106). In considering the use of X-Ray photoelectron spectroscopy (XPS or ESCA) papers dealing specifically with this technique were also reviewed (107,108,109)

Having used I.R. to establish the presence of plasticiser on the surface of a failed bond,it had originally been intended to complement the surface analysis using F.T.I.R. technique following observations by Davidson (110 and

R.A.P.R.A. (111). Technical notes from equipment manufacturers (112, 114) also suggested the possibility of examining the thiol groups and other functional groups of the polymer at the sealant/glass interface. However following trials at Nottingham University and DeMontfort University it was concluded that this technique did not afford the necessary accuracy for these experiments. Consequently only the X.P.S. analysis was carried out.

11.1 DESCRIPTION OF TECHNIQUE

The technique chosen for the surface analysis was ESCA or XPS. This technique is more properly known as X RAY PHOTOELECTRON SPECTROSCOPY and is widely used in adhesion studies. XPS is essentially a non-destructive method which can be used to determine the composition of the outermost elemental layers of a solid. With the exception of hydrogen, all elements can be detected.

XPS is accomplished by bombarding the sample with X-rays of a known energy. Absorption of these X-rays by the sample causes photoelectrons to be emitted, and the kinetic energy of the emitted photoelectrons is determined. The binding energy is determined from the following equation:-

$$BE = hv - KE - Os$$

Where BE is the binding energy associated with the emitted photoelectron, hv is the energy of the X-ray beam, KE is the kinetic energy of the emitted photoelectron and Os is the work function of the spectrometer. The binding energy associated with a peak is then used to establish its elemental identity, examples are shown in the table below.

TABLE 16 BINDING ENERGIES OF SPECIFIC ATOMS

ELEMENT	CHEMICAL SYMBOL	CORE ORBITAL	BINDING ENERGY eV
Carbon	C	1s	285
Oxygen	O	1s	532
Silicon	Si	2p	102
Nitrogen	N	1s	400
Sulfur	S	2p	168

The Carbon 1s peak is used as a reference value for all other peaks.

X.P.S. is also suitable for determining chemical groups on the surface. This is done by deconvoluting the Carbon 1s peak and examining the shifts from 285. The shifts can be attributed to chemical species adjacent to the carbon atom. As there was no confusion over the chemicals present this part of the technique was not used.

The incoming X-rays penetrate a few μm into the surface of the sample. However, the emitted photoelectrons because of

their low kinetic energy (less than 2000 eV), can only travel a short distance without being scattered and losing energy. This short distance is referred to as the escape depth of the electron.

Escape depths range from 5 - 10 nm. depending on the kinetic energy of the electron. The escape depth limitation makes X.P.S. a surface analysis technique .

11.2 EXPERIMENTAL

For the initial analysis a bond was chosen where a high level of adhesion failure had occurred. This was compared to bonds from the same sealant series which had had less ageing and showed cohesive failure, and to bonds also from the same series that had had more ageing. The latter bonds were necessary to ensure that the change to adhesion failure was a real effect and to establish whether any interfacial changes were progressive.

It was the intention to examine the surface where failure had occurred, both on the sealant and on the glass surface. However as the sample size required is only 1 cm^2 the bond is essentially destroyed in order to obtain glass and sealant interfacial surfaces to effect the analysis. The main reason for the bonds destruction being the

difficulty in cutting small samples of glass from the debonded area.

Also because the analysis is carried out in-vacuo one of the early experimental difficulties was ensuring the aged bond was sufficiently dry to allow the vacuum to be applied .

The first tests used formulation X8 and were carried out on bonds that had been aged 1,3 and 10 months, respectively. both surfaces from the failed interface being examined. A typical analysis trace is shown in figure 35 and the relevant data is shown in table 17.

A second test run was carried out on formulation X4 looking at both the glass and the sealant for confirmation.

11.3 RESULTS

The selection of the bonds for surface analysis had been on the basis of an observed transition from cohesive to adhesive failure, that is the initial bonds showed adhesive failure whilst the aged bonds showed cohesive failure. Where possible an intermediate was also selected. The analysis was directed at examination of the sealant surface where failure had occurred, the bulk material close to the

failed surface and the glass surface. The bulk material was an exposed surface within the mass of sealant prepared by cutting through the sealant with a sharp blade.

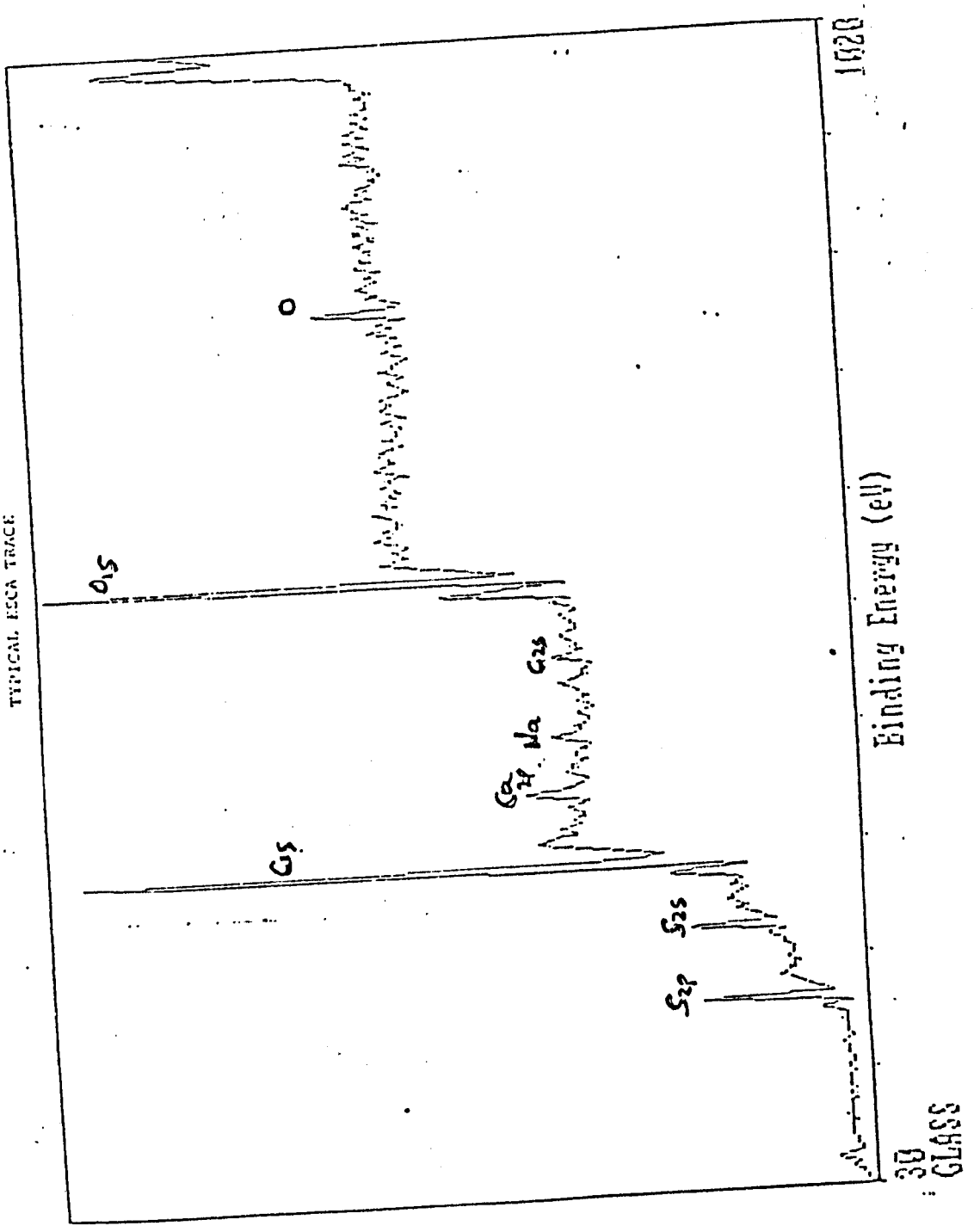
TABLE 17 ANALYSIS TEST DATA

examination of the glass surface by ESCA showing the atomic concentration % at the ageing period indicated from formulation X8

element	peak	1 month	3 month	10 month
sulfur	2p	5.3	3	-
carbon	1s	72.1	66.8	62
oxygen (organic)	1s	19.5	20.4	22.3
magnesium	A	2.1	4.6	3.3
calcium	2p	0.9	1.3	1.6
silicon	2p	-	3	7.7
sodium	A	-	1.1	3

The analysis was directed at looking for variations due to polymer (sulfur), plasticiser (organic oxygen) and filler (calcium). Plasticiser migration would be indicated by an increase in organic oxygen close to the interface.

FIGURE 35 XPS TRACE OF THE GLASS SURFACE AFTER ADHESION FAILURE



The charts and tables (figure 35, table 17) of the analysis indicate a loss of sulfur as adhesion failure increased when the glass surface was examined. This was accompanied by an increase in silicon (glass surface) as shown in figures 36 and 37. This would appear to indicate that adhesion failure progressed by the weakening of the boundary layer which was caused by water diffusion as illustrated by a reduction of polymer at the interface. This was substantiated in part by the loss of sulfur in the 10 month aged sample compared to that of the initial and 4 month result.

It was subsequently discovered that a Brite/Abcon project had been carried out between 1988 to 1991. The work carried out by Centre Scientifique et Technique du Batiment (CSTB) had followed a similar investigation except that the sealant used was a silicone. The glass surfaces were examined by XPS and found to be extremely variable.(159)

Further charts can be found in appendix k.

FIGURE 36 RESULTS OF XPS ANALYSIS SHOWING CHANGES IN ELEMENT CONCENTRATION WITH TIME

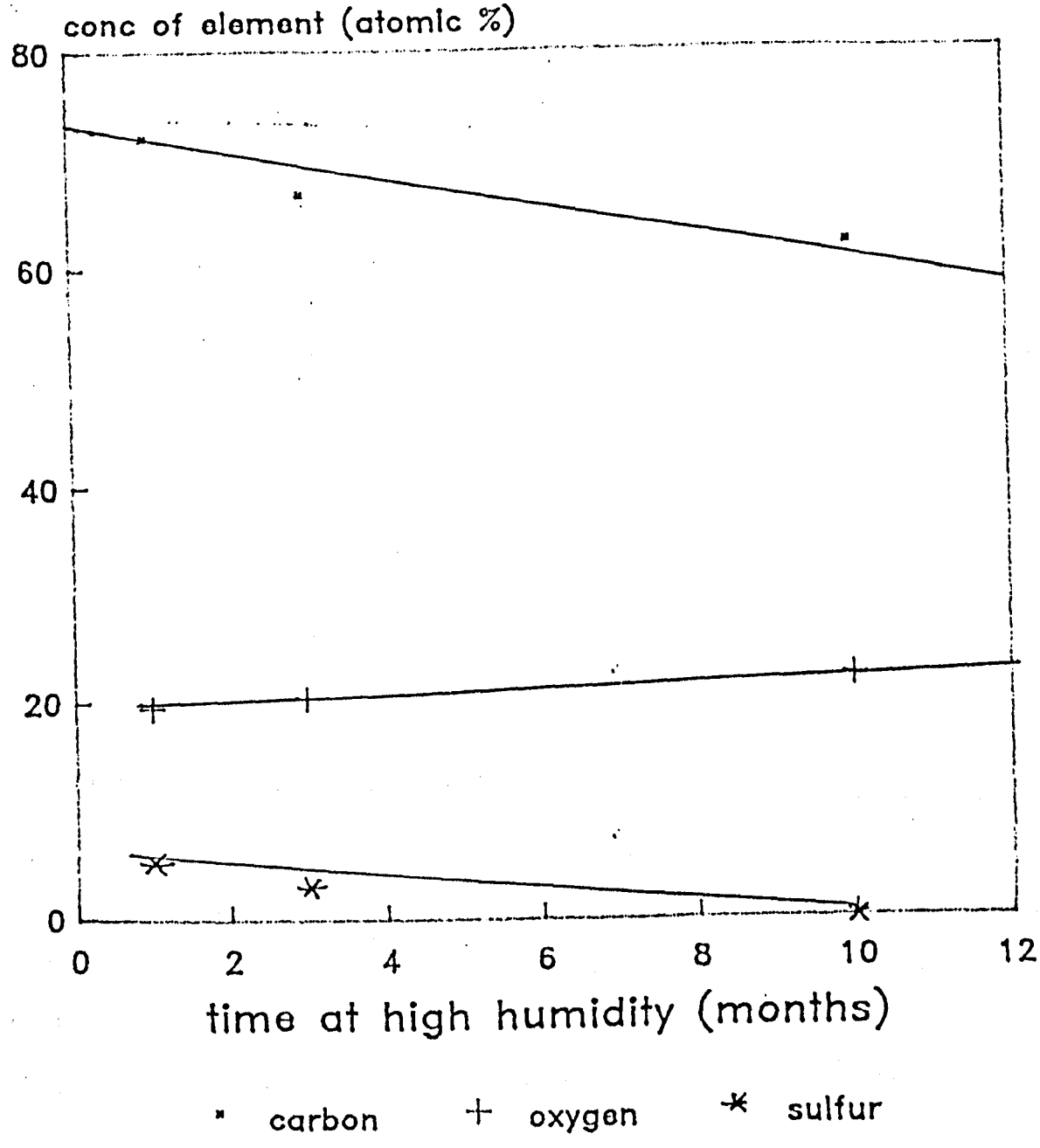
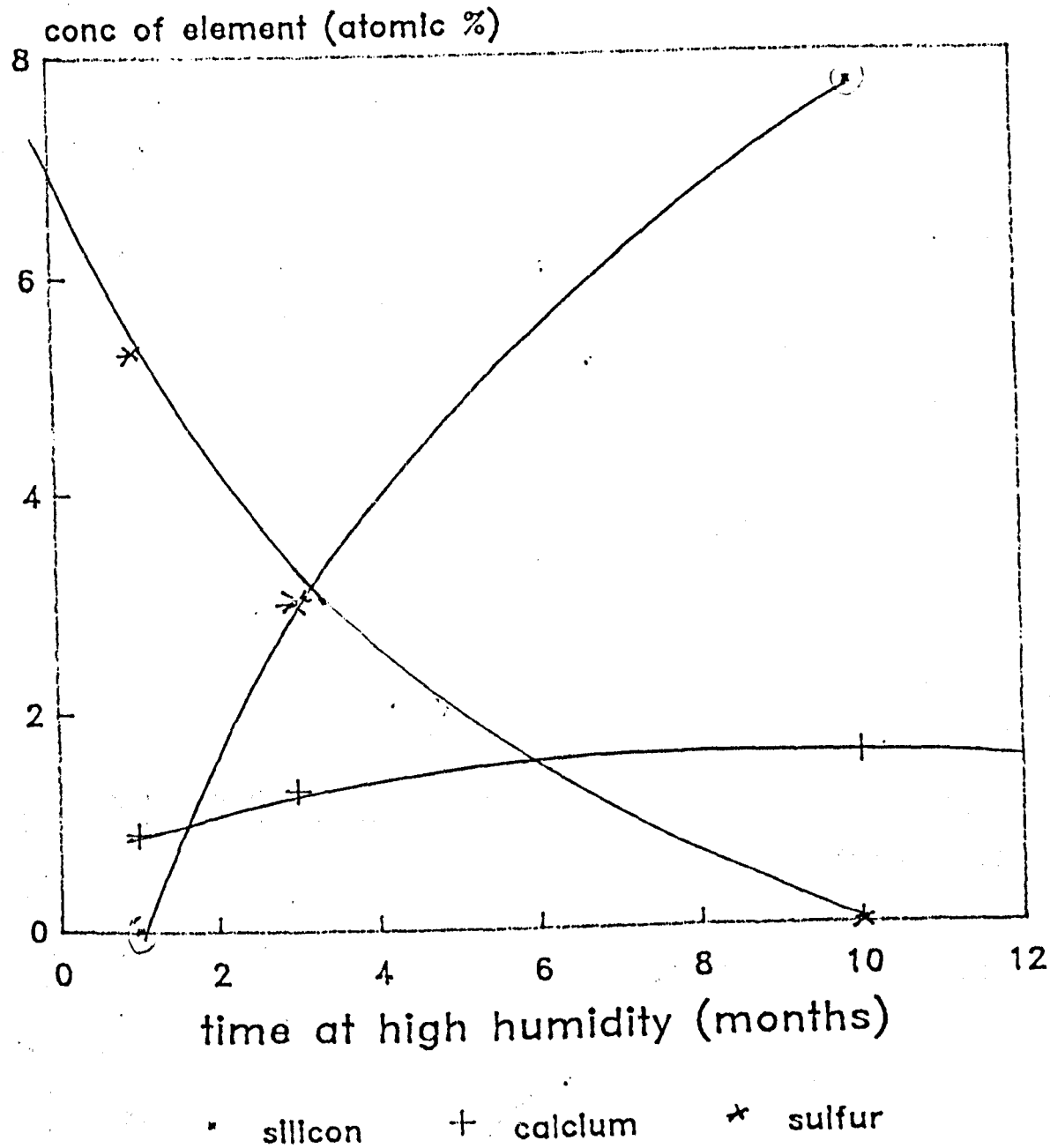


FIGURE 37 RESULTS OF XPS ANALYSIS

as for figure 36



12 POLYMER - PLASTICISER MISCIBILITY

12.1 INTRODUCTION

The blending of polysulfide polymer and phthalate ester plasticiser had earlier been assumed to give total compatibility of mix at all ratios. However due to the lack of initial adhesion with some systems (X5 and X6), as described in section 10.4, believed to be due to plasticiser migration, a simple miscibility study was carried out. This simple experiment was designed to separate the effect from plasticiser migration induced adhesion failure from that of water diffusion induced failure, in that if there was inherent immiscibility the plasticiser would separate from the sealant without influence from water diffusion.

12.2 TEST METHOD AND RESULTS

Blends of polymer - plasticiser and silane, in the ratios used in formulations X1 - X10 as described in section 5.1.1 tables 3a and 3b were prepared. These were mixed thoroughly together and allowed to stand for 7 days at 23^0 C and 50% R.H. to remove air bubbles caused by stirring. Any separation was noted visually. The containers with the blends are shown in plate 7.

An extra mix, designated X11, was prepared using a polymer

PLATE 7 CONTAINERS SHOWING THE POLYMER/PLASTICISER BLENDS USED FOR COMPATIBILITY TESTS

to plasticiser ratio of 1:2.

The mixes were compatible except for X11 which showed two distinct layers after standing. Following the initial observations the mixes were placed in a cooling chamber, controlled at 6°C, for 24 hours. After this time the containers were again inspected for signs of incompatibility.

Mixes X6 and X10 had gone cloudy after the low temperature treatment indicating immiscibility. Comparisons with the adhesion testing shows that both X6 and X10 had poor initial adhesion. X11 again remained as two separate layers after the low temperature treatment, X6 is shown in plate 8 and X11 in plate 9.

PLATE 8 COMPATIBILITY TEST SHOWING IMMISCIBILITY AND SEPARATION AFTER LOW TEMPERATURE TREATMENT

X6 showing cloudiness

PLATE 9 COMPATIBILITY TEST

X11 showing separation after low temperature treatment

13 THERMODYNAMIC WORK OF ADHESION

13.1 INTRODUCTION TO THERMODYNAMICS OF ADHESION

There are a number of theories of adhesion. These have been discussed by Wake (115) and by Kinloch (116) and (70)), with further industrial examples given in the book by Brewis and Briggs (117). The situation was also covered briefly by Heath (120) in his article on coatings.

The theories most frequently referred to in the literature include mechanical interlocking, diffusion, adsorption, electrostatic bonding weak boundary layers and chemical bonding.

Of these many theories, that relating to mechanical interlocking via surface roughness is probably the oldest, and is evident in such applications as textile bonding. For this work, as all the bonds used glass as the test surface, the surface topography was not a relevant factor in the changes in adhesion. It has also been stated by a number of workers that modern float glass is optically flat and therefore surface roughness need not be considered.

The diffusion theory assumes sufficient molecular mobility at the adhesive-adherend interface to allow the diffusion to take place. Aubrey and Beech (119) had tried to investigate this with building and construction sealants based on polysulfides at the macro level by making a boundary layer of a

mixture of primer and sealant. In this case however the results were not conclusive.

Little information was available in the literature involving polysulfides in studies covering these theories.

Meanwhile Zisman had introduced the concept of critical surface energy, whilst Dupre' used work of adhesion and Young examined the relationship between surface tension and surface energy.

Contact angle measurements using liquids of known physical properties can be used to investigate surface properties of both adhesive and adherend, and the knowledge thus gained can be used to investigate van-de Waals forces acting at the interface.

The properties of surface tension and contact angle were therefore considered to be the most appropriate to investigate in this work. As the choice of formulating ingredients remained the same for all formulations with only the ratios varied it was thought that the wetting of the glass surface, and hence the properties of the sealants affecting wetting could affect adhesion and would seem to be the most appropriate feature to study.

13.2 INTRODUCTION TO CONTACT ANGLE AND WETTABILITY

A useful introduction to this subject was written by Shanahan (161) in Rubber World.

When a liquid is placed on a solid a new interface is formed, liquid/solid which replaces the liquid/air and solid/air interfaces. It can be shown that the reversible free energy change G_{sl} per unit area of new interface formed is

$$G_{sl} = \tau_s - \tau_{sl} - \tau_{lv} = - W_A$$

where τ_{sl} = the interfacial tension

τ_s = surface free energy of the solid in vacuum

τ_{lv} = surface tension of liquid in equilibrium with its vapour

W_A = thermodynamic work of adhesion

The contact angle is a measure of the extent of wetting of the solid by the liquid and is described more fully in this section. The contact angle is measured at the three phase boundary between the liquid, solid surface and air. When a liquid wets a solid to the extent that the contact angle becomes

zero the liquid is said to spread. The equilibrium spreading coefficient S is defined as

$$S = \tau_{sv} - \tau_{sl} - \tau_{lv}$$

A liquid will spread spontaneously when $S \geq 0$

It has been argued (70) that for good adhesion of a sealant to a substrate the contact angle must be zero. However if adhesion only occurred when the contact angle was zero then the use of adhesives would be severely limited.

A number of problems exist. For example it is not known what energy changes occur as the sealant changes from liquid to solid and what if any are the changes on ageing. Also any differences occurring between a surface cured when exposed to air compared to the sealant surface cured against glass. A recent article by Gutowski (120) has suggested only the uncured properties should be considered.

Huntsberger (116) suggested that because most surfaces were irregular it would be more appropriate to consider the free energy changes necessary to obtain complete wetting of the surface as given by

$$G_{sl} = -\tau_{lv}(1 + (\Omega_s / A_s) \cos\Theta$$

Where (Ω_s / A_s) is the ratio of the actual area to projected area of bond surface , which indicates that adhesion can occur even if the contact angle Θ is greater than zero.

There are a number of authors who have explored the relationship between surface tension, contact angle and wetting of surfaces , and the usefulness of determining these parameters in understanding adhesion technology.

Bascom (121) explored the relationship between wettability and contact angle determination, expanding the original work of Zisman. He argued that by combining Youngs equation

$$\text{Cos } \Theta = \frac{\tau_{sv} - \tau_{sl}}{\tau_{lv}}$$

where Cos Θ is the contact angle

τ_{sv} = surface tension of solid

τ_{sl} = interfacial tension between solid and liquid

τ_{lv} = surface tension of liquid

with that of work of adhesion of Dupre' can be calculated

$$W_A = \tau_{sv} + \tau_{lv} - \tau_{sl}$$

yields the Young-Dupre' equation

$$W_A = \tau_{lv} (1 - \text{Cos } \Theta)$$

It was then argued that the work of adhesion (W_A) can be separated into dispersive and polar interactions using the harmonic mean (HM) approximation and the geometric mean (GM) approximation.

$$\gamma_{lv}(\text{Cos}\,\Theta + 1) = \frac{4\gamma_{sv}^{d}\gamma_{lv}^{d}}{\gamma_{sv}^{d} + \gamma_{lv}^{d}} + \frac{4\gamma_{sv}^{p}\gamma_{lv}^{p}}{\gamma_{sv}^{p} + \gamma_{lv}^{p}} \quad \text{(HM)}$$

$$\gamma_{lv}(\text{Cos}\Theta + 1) = 2(\gamma_{sv}^{d}\gamma_{lv}^{d})^{1/2} + 2(\gamma_{sv}^{p}\gamma_{lp}^{p})^{1/2} \quad \text{(GM)}$$

Wu (130) states that the harmonic mean equation is more suitable for low energy materials. The geometric mean attributed to Fowkes (128) is claimed to be preferred when using materials of dissimilar polarity. Good (122) examined the intermolecular and interatomic forces and many workers have used his work for the basis for expansion of other theories.

The Good-Girifalco equation uses the molecular interaction theory to give an interaction parameter ϕ where

$$\phi = \frac{Wc1.2}{(Wc1\ Wc2)1/2}$$

where Wc is the molecular interactions of surfaces 1 and 2 and the intersurface reaction 1.2 respectively

taking $Wa = \gamma_1 + \gamma_2 - \gamma_{12}$

and combining the two equations gives

$$\phi = \frac{\gamma_1 + \gamma_2 - \gamma_{12}}{2(\gamma_1\gamma_2)^{1/2}}$$

combining this with the Young equation gives

$$\text{Cos}\Theta = 2\phi(\gamma_{sv}/\gamma_{lv})^{1/2} - 1$$

Gent and Schultz (123) followed the above arguments in examining adhesive strengths, whilst Fowkes (124) studied the acid -base interactions in polymer adhesion. Similarly Kaelble and Uy (125) also used Good-Young and Zisman equations to study liquid - solid surface interactions.

Other workers dealing with the broad concept of surface thermodynamics include Owens(126, 127), Fowkes (128) and Range (129).

Wu (130) in his book covers the theory of contact angle and wettability extensively.

Three experimental avenues were explored, surface tension of the liquid phase, contact angle measurements,and the interfacial surface tensions of the liquid ingredients, and the data obtained examined with reference to the adhesion test results.

13.3 MEASUREMENT OF LIQUID SURFACE TENSION

13.3.1 TORSION BALANCE

The most commonly used technique for measuring surface tension is to use the ring pull method employing a torsion balance.

The basis for the method was developed by Harkins and Jordan (131) . They argued that the lack of accuracy originally attributed to the ring pull method was due to the false presumption that the maximum force P on the ring was given by

$$P = 4\pi R\tau$$

where R = radius of the ring measured from the centre of the ring to the centre of the wire and τ a function of surface tension.

By varying the ring size and other variables within the system and then comparing the surface tension values obtained with those obtained by the capillary height method (a method used to determine the surface tension of pure liquids by measuring the height of the liquid in a capillary of diameter 0.02557 cm. compared to that in a large tube of diameter 1.805 cm.) using pure liquids they found that their results were accurate and met the conditions predicted when corrections were applied to the above equation . This gives rise to the following equation for surface tension.

$$\tau = \frac{pF}{4\pi R}$$

where

$$F = f\left(\frac{R^3}{V} x \frac{R}{r}\right)$$

τ = surface tension

F is a correction factor and values for these are listed in Harkins and Jordan

r = diameter of the ring wire.

Thus F and R are ring constants.

It had been suggested by Harkins and Jordan that the ring pull method of determining surface tension could be in error by as much as 30% (131). However Freud and Freud proposed that the ring pull method could be 'considered an absolute one for the determination of surface tension' (162).

The tests were carried out on the liquid phase of the sealant systems using a torsion balance manufactured by White Electric Instrument Co. Some of the values obtained were on an apparatus kindly loaned by Taywood Laboratories, whilst later results were obtained on apparatus available at Morton International.

13.3.2 EXPERIMENTAL DETAIL AND RESULTS OF MEASUREMENTS

The test liquids relating to the base systems X1 to X10 as described in the sealants section 5.1 were stored at 23 °C and 50% R.H. for 24 hours to stabilise.

Due to lack of availability of the torsion balance the liquids were left to stand for 3 weeks. After this period it was noted that X6 and X10 had both separated, as had another system that was produced to extend the series and was designated X12. This had a polymer/plasticiser ratio of 2/1. The results are shown in table 18 below;

TABLE 18 SURFACE TENSION MEASUREMENTS

formulation of base	SURFACE TENSION (mNm^{-1}) of uncured formulations		
X1	53		
X2	38.4		
X3	38		
X4	37		
X5	35.5		
X6	37.25(TL)	38.5(MIX)	5(I)
X7	40		
X8	43.5		
X10	35(TL)	38.5(MIX)	5(I)
X12	37(TL)	39(MIX)	5 (I)
POLYMER (Thiokol LP2)	53		
PLASTICISER (santicizer 278)	37		

TL = top layer, MIX = mixed layers, I = interfacial tension between the polymer and plasticiser where separation had occurred (these relate to those systems showing separation)

Following these tests the interfacial tension between the polymer and water and that between plasticiser and water was measured by carefully preparing a two phase system and measuring the tension between the two liquids. The technique used was to place the ring just below the interfacial boundary and allow the system to settle before carefully drawing the ring through the separation layer. The results are given in table 18a.

TABLE 18a INTERFACIAL TENSION mNm^{-1}

polymer/water	28
plasticiser/water	20

13.4 CONTACT ANGLE MEASUREMENT

In association with the work on surface tension and the thermodynamics of adhesion, it was necessary to evaluate the contact angles, using standard liquids, on the cured films of the sealant systems under evaluation.

The use of contact angle data in adhesion science is covered by Kinloch (116) and Wu (130). Further evidence of its use and interpretation was

found in works by Zvonar (132) and Andrade et al (133) who described a number of techniques for measuring contact angle.

Further evidence of the use of contact angle measurements and its use in adhesive performance technology is found in the work of Penn (134), Head (135) and Briggs et. al. (136).

A drawing together of the various techniques for adhesion/adhesive interface thermodynamics was given by Mora et.al. in their article entitled "Knowledge about polymer surfaces from contact angle measurements" (137). The fact that information on surface tension and contact angle is still useful can be determined by the many recent articles covering a wide range of adhesive disciplines. Typical examples of such articles are those by Brewis (138), Svhnall (139) and Tsutsumi et. al. (140).

For the measurements of contact angle a Kruss goniometer was kindly made available by the Institute of Polymer Technology and Materials Engineering at Loughborough University. The standard liquids together with their thermodynamic properties used in the experiments are shown in table 19, the selection of the liquids and their properties were taken from Kinloch (116).

TABLE 19 SURFACE TENSION, POLAR AND DISPERSIVE FORCES OF TEST LIQUIDS in mNm^{-1}

(these liquids are used in contact angle measurements)

	γl	γld	γlp
dimethyl formamide	37.36	32.42	4.88
dimethyl sulphoxide	43.54	34.86	8.68
ethane diol	48.3	29.3	19.0
water	72.8	21.8	51.0

where γl = surface tension and γld and γlp are the dispersive and polar forces respectively.

13.4.1 DETERMINATION OF CONTACT ANGLES

Cured films of the sealant systems were prepared by casting onto a non adherend (polyethylene) surface. The films thus produced were used as the platform on which to dispense small drops of the test fluid.

After applying a drop of liquid onto the surface the drop was brought into focus by adjustment of the base support of the goniometer and the contact angle obtained by adjustment of the optical cross wires centred at the point of contact between the liquid and the test surface .

The view through the goniometer can be either of the two types shown in figure 38.

In order to ensure that the surface properties were not affected by exposure to air during cure, some films were tested on both the exposed surface and the cast surface. Also an unused glass surface was tested using the same test liquids, in this case both sides of the glass were tested to ensure there was no variation due to the float method of manufacture.

13.4.2 CONTACT ANGLE RESULTS

The surface tension properties of the test liquids given in table 19 above are used to calculate the X and Y parameters for the Fowkes plots described below. When the drop of liquid forms on the solid sealant surface the shape so formed depends on the wettability of the liquid on that surface. The drop shapes are shown in figure 38. Three determinations were made on each test surface and the results quoted are an average of the three readings. It was possible to determine the contact angle with an accuracy of +/- 2deg. The average results in tabular form are given below in table 20 .

From the above results were plotted in the following form,

$$\text{Y axis} = \frac{\tau_{sl}(1 + \cos\theta)}{2\sqrt{\tau(_l^d)^{1/2}}}$$

$$\text{X axis} = (\tau_l^p/\tau_l^d)^{1/2}$$

this gives Intercept $= (\tau_s^d)^{1/2}$

Slope $= (\tau_s^p)^{1/2}$

where τ_s^d and τ_s^p are the dispersive and polar constituents of the cured films surface energies.

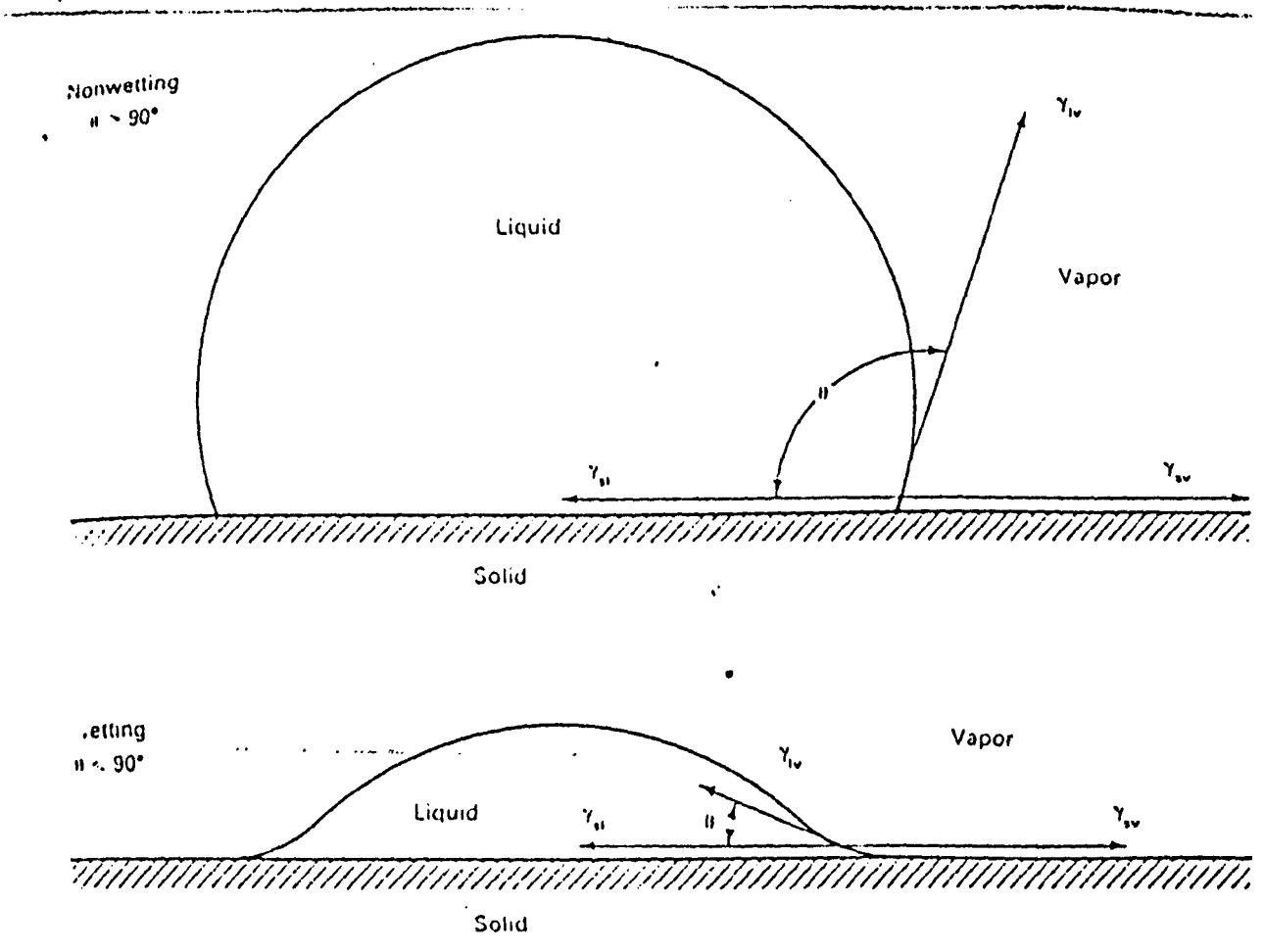
The graphs known as Fowkes plots are shown in figures 39 to 41, errors in the Y coordinate of each point are low because of the reproducibilty of individual contact angle measurements.

The derivision of the above is taken from the geometric mean equation (page 140) and rearranging to give

$$\frac{\tau_{lv}(1+\cos\theta)}{2(\tau_l^d)^{1/2}} = (\tau_s^d)^{1/2} + (\tau_s^p\tau_l^p/\tau_l^d)^{1/2}$$

which is a straight line equation of intercept $(\tau_s^d)^{1/2}$ and slope $(\tau_s^p)^{1/2}$ can be derived.

FIGURE 38 SHOWING TYPES OF DROP FORMATION AS SEEN THROUGH A GONIOMETER



Sessile drop configuration

TABLE 20 CONTACT ANGLE MEASUREMENTS (degrees)

	TEST LIQUID		
sealant	water	ethane diol	dimethyl sulphoxide
X1	71	52	28
X2	70	64	17
X3	75	57.5	15
X4	78	61	18
X5	72	60	12
X6	-	-	-
X7	59	59	18.5
X8	70.5	56	20
X9	62.5	44	17
X10	65	53	12
CONTROL	75	43	29

note the control is cured polysulphide only, there is no filler, pigment or thixotrope present. No results are shown for dimethyl formamide due to its spreading, thus the contact angle $\Theta = 0°$

From the intercept and slope of these graphs the following data, listed in table 21, was obtained, the values were confirmed and the errors calculated by using the least mean square calculation (see appendix)

TABLE 21 SURFACE PROPERTIES OF TEST FILMS

sealant	$\gamma s^d (mJm^{-2})$	calculated error (mJm^{-2})	$\gamma s^p (mJm^{-2})$	calculated error (mJm^{-2})
X1	11	4.7	25.9	3.3
X2	24.8	10.5	11	7.7
X3	29.4	7.3	7.4	4
X4	30.6	7.9	5.6	3.7
X5	27.2	9	9.3	5.7
X7	19.3	9.8	20.9	11
X8	26.1	7.1	10.8	4.9
X9	23.4	4.5	17.5	4.2
X10	24	7.4	15	6.3
control	29.8	0.3	8.1	0.2

It will be seen from the contact angle determination results (table 20) that

the result for X1 more closely matches that of the control sample than it does the results of the formulation series.

The control film has no plasticiser and it is concidered that the apparently anomolous result of X1 is due to its very low plasticiser level, such that there is little influence on the properties of the cured film by that plasticiser.

Following the tests on the cured films the contact angle was measured on a clean glass surface. The glass sample was taken from the same batch of test pieces as those for the adhesion tests. The following average contact angles were measured :-

test liquid	contact angle Θ° (deg)
water	17.5
ethane diol	28
dimethyl sulphoxide	17.5
dimethyl formamide	10

No significant difference was noted between the two sides of the glass. The concern of the effects of the different sides of glass arises from the method of production where the float system is used.Float glass is produced by floating the molten glass ribbon on a bath of molten tin. This process gives an optically flat surface, the upper surface is maintained in a reducing atmosphere to prevent surface oxidation at the melt

temperature.

From the graphical/mathematical interpretation, (figure 42) explained above, the surface properties of glass were found to be :-

intercept	$\gamma s^d (mJm^{-2})$	slope	$\gamma s^p (mJm^{-2})$
4.0	16 +/-5	6.9	47+/13

The data obtained by the various thermodynamic determinations described above can be used to calculate the thermodynamic work of adhesion.

These results were found to be similar to those obtained in the Brite project (ref 113) where the dispersive component values ranged from 6 to 86 mJm^{-2} and the polar component values were 3 to 40 mJm^{-2}. These show a very wide variation concidering that glass is normally regarded as a standard surface.

FIGURE 39 FOWKES PLOTS FOR FILMS

films are control,X1,X2, and X7

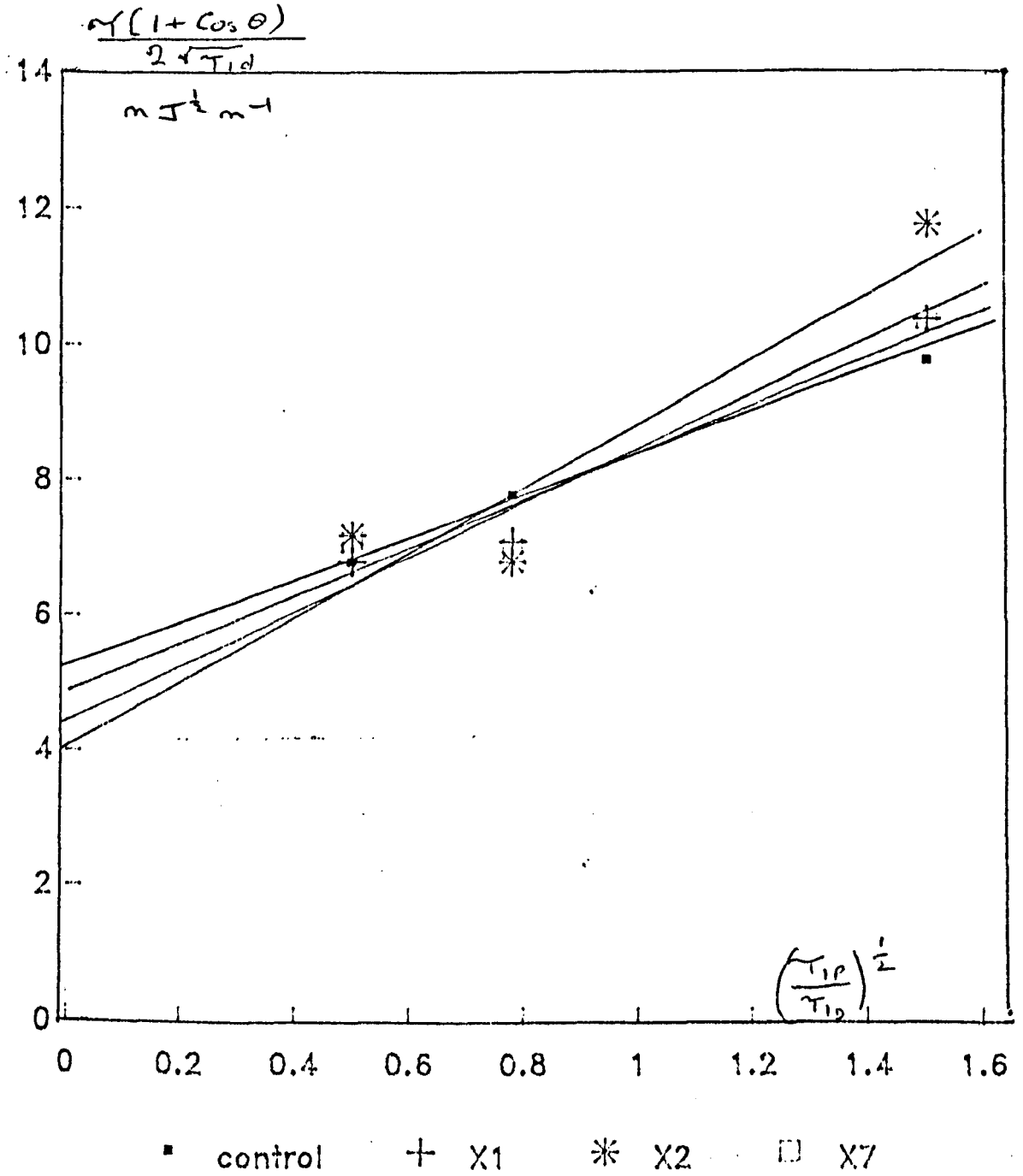


FIGURE 40 FOWKES PLOTS FOR FILM

films are X3, X4, X8, and X9

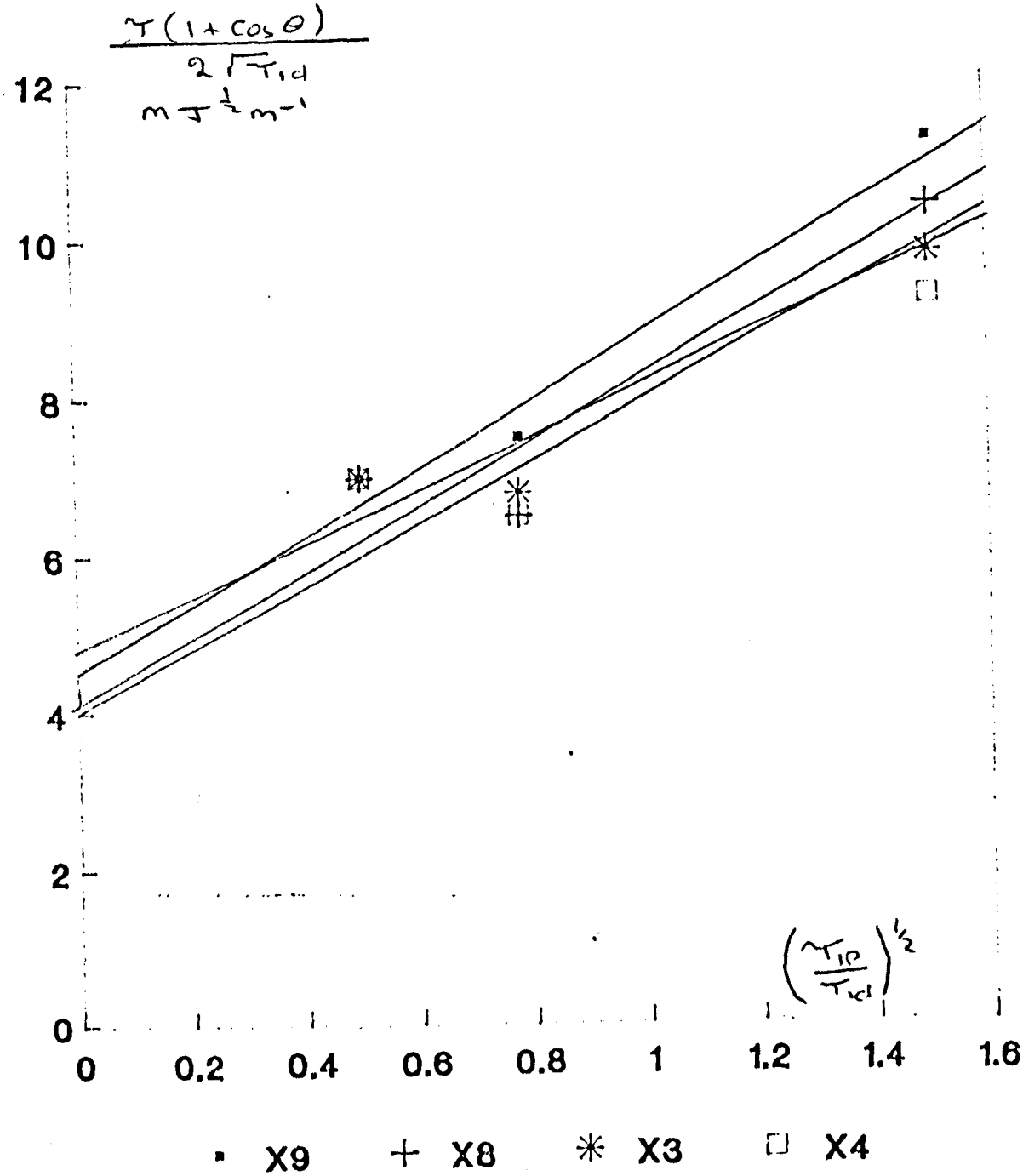


FIGURE 41 FOWKES PLOTS FOR FILMS

films are X5 and X10

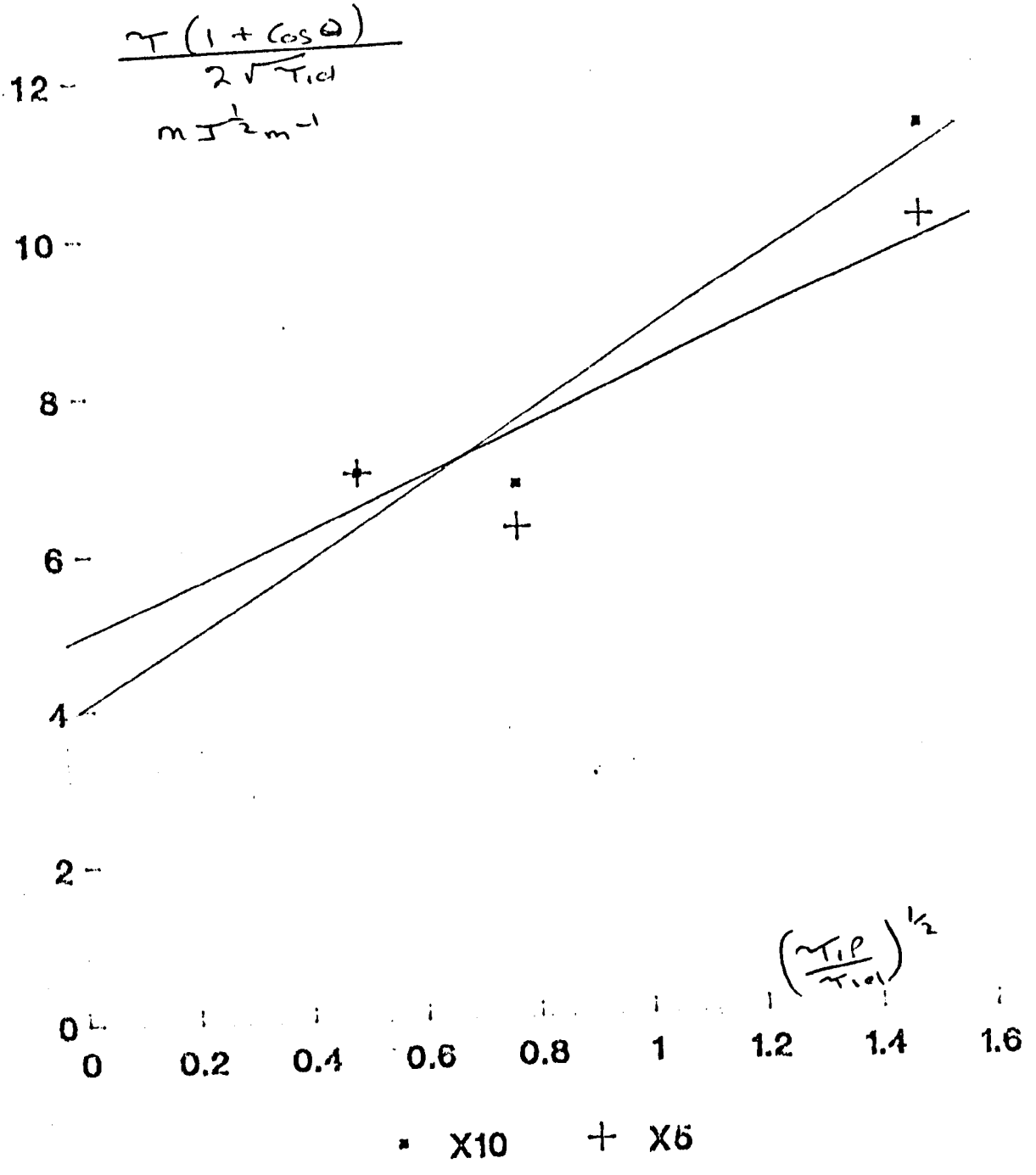
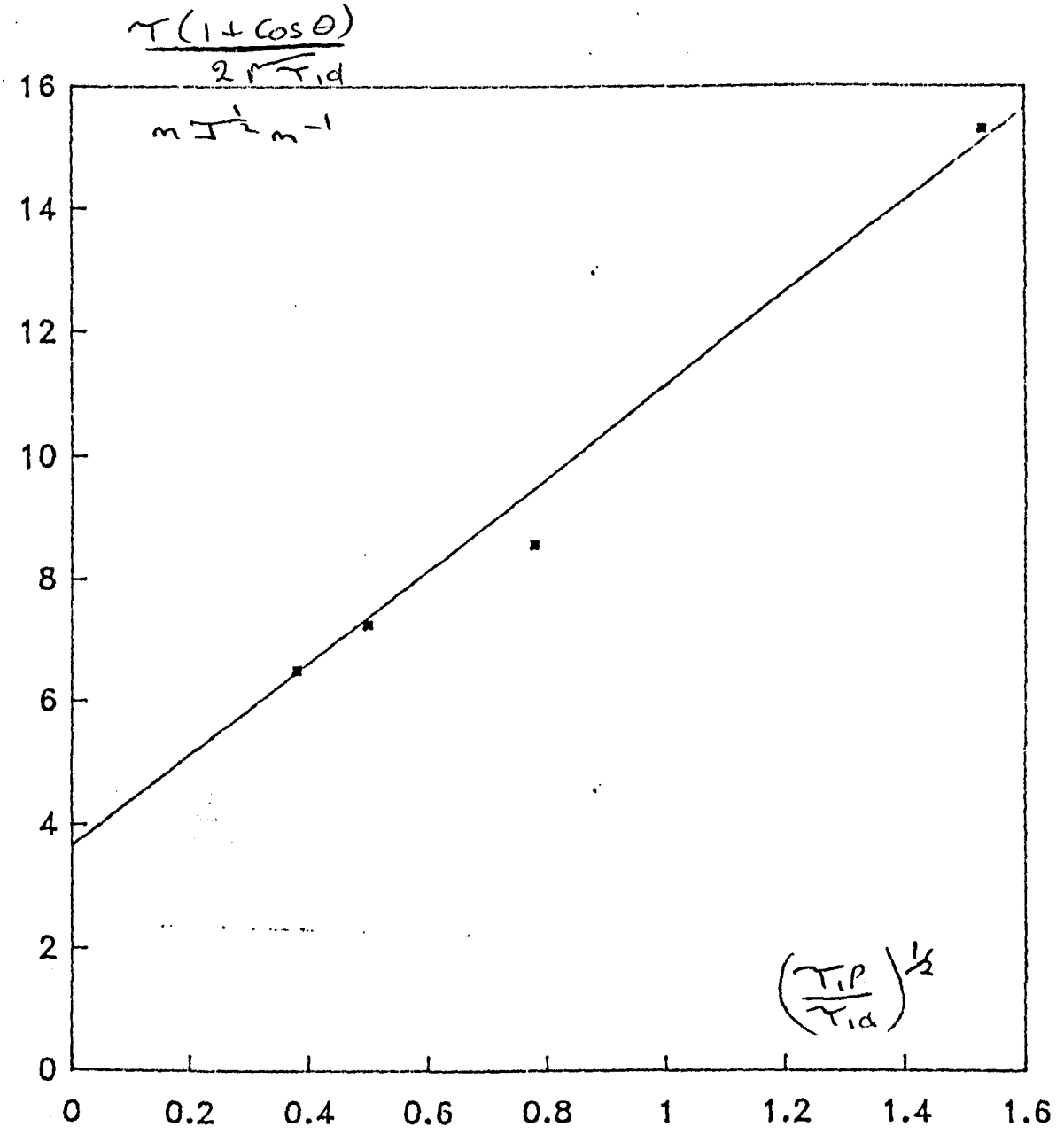


FIGURE 42 FOWKES PLOT FOR GLASS SURFACE



13.5 CALCULATIONS OF WORK OF ADHESION

Prior to calculating the work of adhesion and the use of other thermodynamic data it was decided to examine the relationship between the sealant formulations and the surface energy properties.shown in table 21. Graphs of the polar component versus the polymer plasticiser ratio and dispersive component versus the same parameter showed little evidence of a direct relationship, as can be seen in figures 43 and 44 respectivelv. Errors in these points are quite high: they are given in Table 21 and are typically ±7 mJm^{-2}.

From data obtained via contact angle determinations it is possible to calculate the work of adhesion of the system.

As discussed earlier in this section the work of adhesion Wa is given by

$$Wa = \tau_{sv} + \tau_{lv} - \tau_{sl}$$

the definitions are as section 13.2 page 137

A computer programme was prepared to simplify the repetitive calculations and is given in the appendix.

The results show very little variation within the range of systems tested as shown in table 22 and figure 45. It should be noted that for these calculations the dispersive and polar components of the substrate are those obtained from experiment

FIGURE 43 GRAPH SHOWING EFFECT OF POLYMER/PLASTICISER RATIO ON DISPERSIVE COMPONENT OF THE SOLID SEALANT

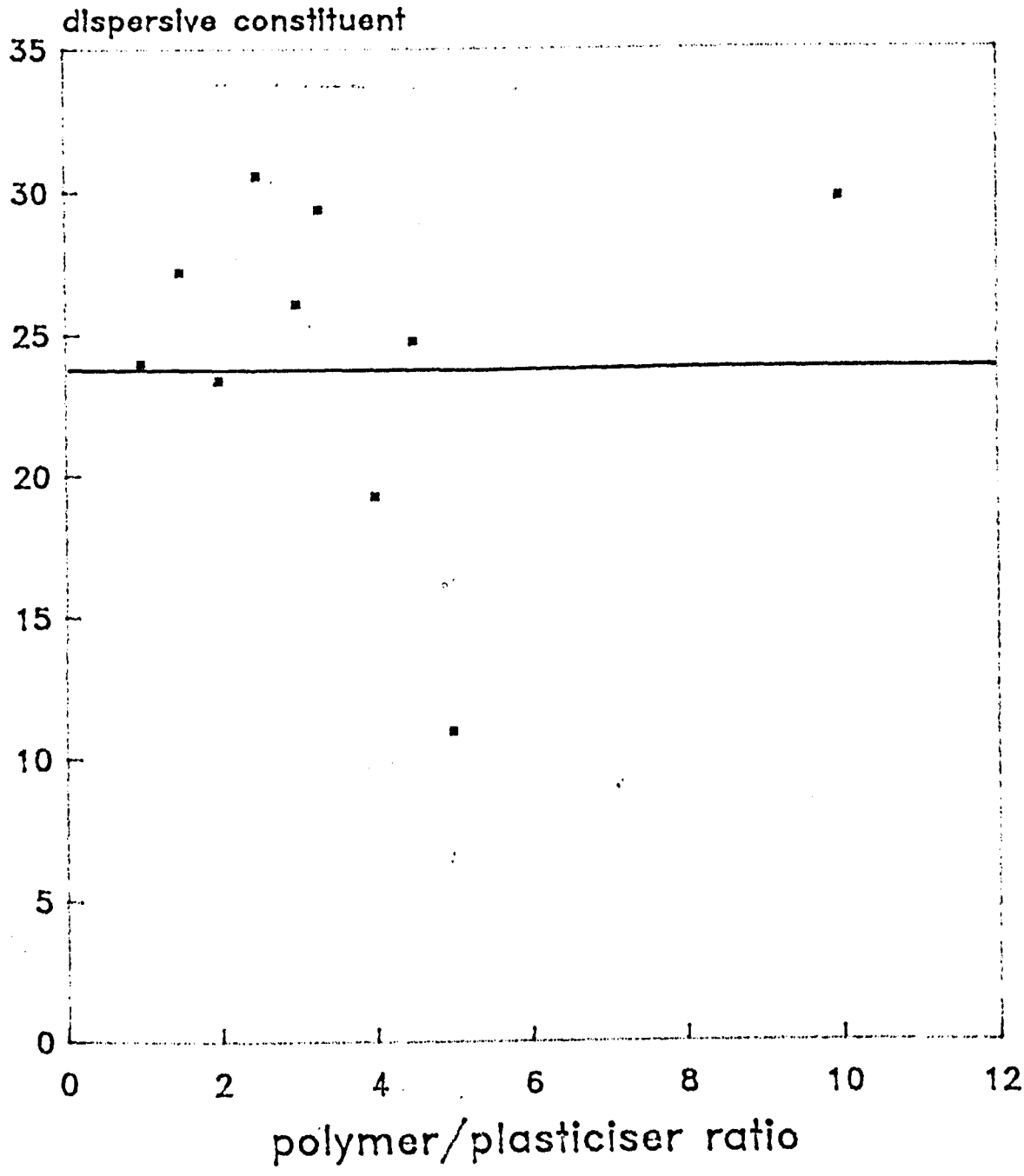


FIGURE 44 GRAPH SHOWING EFFECT OF POLYMER/PLASTICISER RATIO ON POLAR COMPONENT OF THE SOLID SEALANT

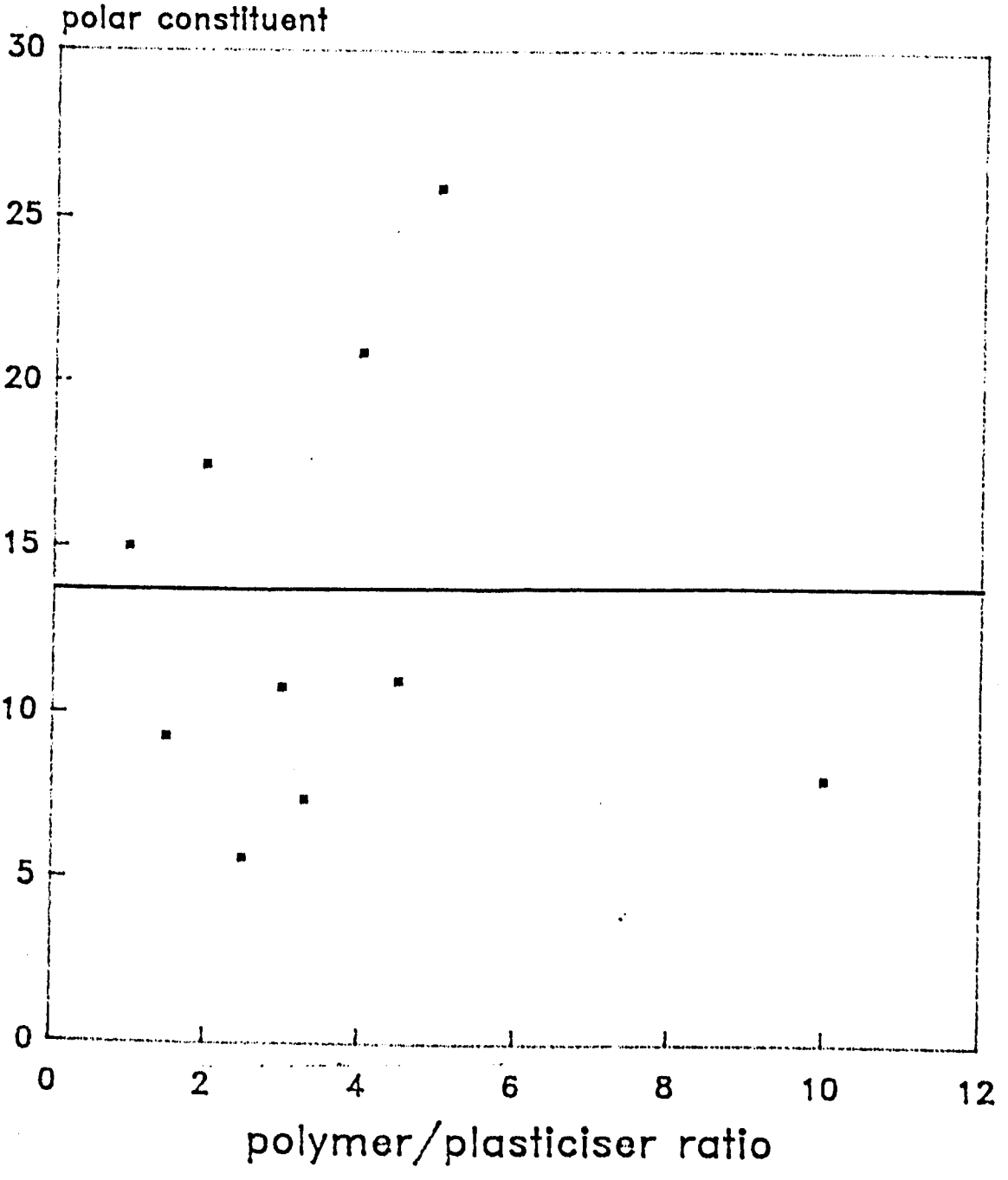
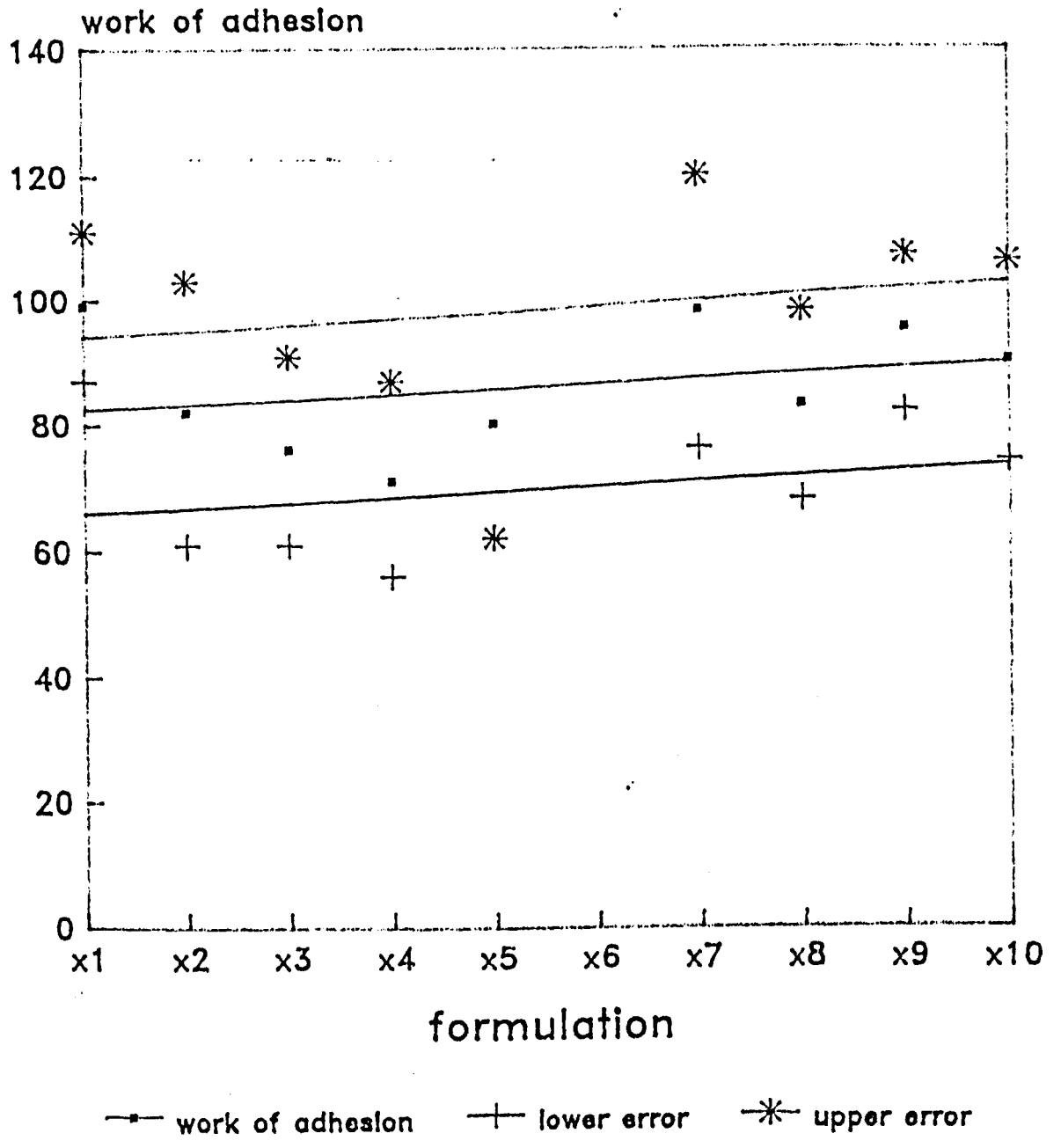


FIGURE 45 WORK OF ADHESION IN THE DRY FROM CONTACT ANGLE DETERMINATIONS

showing error bars



and not ones taken from literature.

TABLE 22 CALCULATED WORK OF ADHESION IN THE DRY

SEALANT FORMULATION	WORK OF ADHESION mJm^{-2}
XI	99 +/-12
X2	82 +/-21
X3	76 +/-15
X4	71 +/-16
X5	80 +/-18
X7	98 +/-22
X8	83 +/-15
X9	95 +/-13
X10	90 +/-16

It would appear that the work of adhesion is independent of sealant formulation. This data was a little surprising in that it did not indicate that a major failure would occur even with formulations comprising high levels of plasticiser. The above expression for work of adhesion can be modified to take into account the presence of water. The relevant equation is given below and requires a knowledge of surface tension and dispersive component of the liquid (water) in question.

In the first instance the liquid is water and therefore the values of surface tension and dispersive component are those given in table 19 and are as follows

surface tension	72.8
dispersive component	21.8
polar component	51.0

By inserting these values into the following equation the work of adhesion in the wet can be obtained.

$$Wa = 2(\tau_L^D+\tau_L^P) - (\tau_A^D*\tau_L^D)^{1/2} - (\tau_A^P*\tau_{LP})^{1/2} - (\tau_S^D*\tau_L^D)^{1/2} - (\tau_{SP}*\tau_L^P)^{1/2} + (\tau_A^D*\tau_S^D)^{1/2} + (\tau_A^P*\tau_S^P)^{1/2}$$

The calculations yielded the following results as given in table 23 and figure 46.

These results show a considerable drop in the value of the work of adhesion when compared to the values obtained for the dry bonds. They were however still independent of formulation, and remained positive indicating that the presence of water alone is not sufficient to cause adhesion failure.

A further extension of the above is to consider the liquid present to be one of the constituents of the system. In this case the most likely free liquid would be the plasticiser.

FIGURE 46 WORK OF ADHESION IN THE PRESENCE OF WATER CALCULATED FROM CONTACT ANGLE DETERMINATIONS FOR SEALANT FORMULATIONS

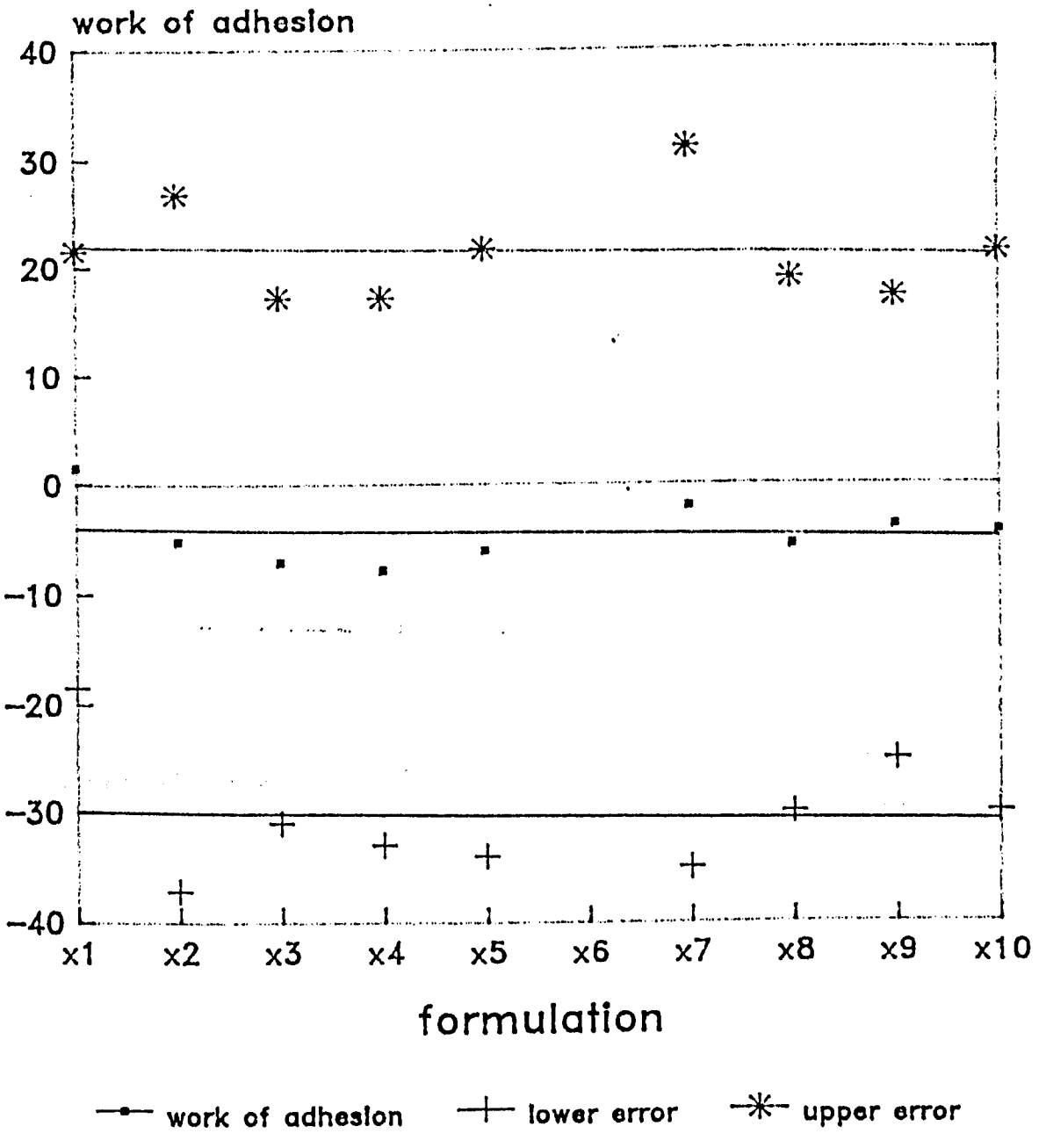


TABLE 23 WORK OF ADHESION IN THE PRESENCE OF WATER

SEALANT FORMULATION	WORK OF ADHESION mJm^{-2}
XI	1.5 +/-20
X2	-5 +/-32
X3	-7 +/-24
X4	-8 +/-25
X5	-6 +/-28
X7	-2 +/-33
X8	-6 +/-24.5
X9	-4 +/-21
X10	-4.5 +/-26

The values required for this calculation are the dispersive and polar components of the plasticiser. These can be derived from the surface tension and interfacial tension between the plasticiser and water. These values had been obtained earlier and are given in tables 18 and 18a.

The surface tension of the plasticiser was found to be 37, and the interfacial tension between plasticiser and water was 20 mjm^{-2}.

By incorporating known values into the equation below, the dispersive and polar component can be calculated.

$$\tau_{1.2} = \tau_1 + \tau_2 - 2(\tau_1^D * \tau_2^D)^{1/2} - 2(\tau_1^P * \tau_2^P)^{1/2}$$

In order to resolve the above it was necessary to obtain a

second set of values where τ^D and τ^P would be known. The surface tension of a silicone oil together with its interfacial tension with the plasticiser was measured as 18.5 and 4 respectively. It was assumed that the silicone oil was substantially non polar and therefore $\tau^P = 0$. It was then possible to incorporate all the known values into simultaneous equations.The dispersive component of the plasticiser τ_2^D can then be deduced. Then by using the relationship

$$\tau_2 = \tau_2^D + \tau_2^P$$

the polar component of the plasticiser τ_2^P can be calculated.

$\tau_2^D = 23$ and $\tau_2^P = 14$ for the plasticiser

These values can now be incorporated into the work of adhesion in the presence of a liquid equation above . The values thus obtained are shown below in table 24.

These values are within experimental error the same as for the results obtained for the work of adhesion in the presence of water, and therefore it can be concluded that the plasticiser itself could be responsible for the adhesion breakdown as well as water.

TABLE 24 WORK OF ADHESION IN THE PRESENCE OF PLASTICISER

SEALANT FORMULATION	WORK OF ADHESION mJm^{-2}	+/-ERROR
X1	-5	17
X2	-6	27
X3	-10	20
X4	-11.5	20
X5	12.5	23
X7	6	28
X8	-5	20
X9	0.5	17
X10	7	21

A similar sequence of calculations can be carried out for the pure polymer and using values from table 18 and 18a These yield SURFACE TENSION 53 mNm^{-1}

DISPERSIVE COMPONENT 50 "

POLAR COMPONENT 3 "

In the case of the polymer, only fractional lowering of the work of adhesion is noted (table 25).

The results of the calculations of work of adhesion in the presence of water and that for plasticiser would indicate very little difference between the two components, and therefore if this were the only consideration all the

systems would fail at approximately the same rate.

However as was seen in the surface analysis, chapter 11, the plasticiser increases in concentration at the surface and therefore the mobility of the liquids within the system has to be considered.

TABLE 25 WORK OF ADHESION IN THE PRESENCE OF POLYMER

SEALANT FORMULATION	WORK OF ADHESION mJm^{-2}
X1	91
X2	105
X3	83
X4	79
X5	88
X7	109
X8	91
X9	102
X10	98

The computer programme for the calculating of the work of adhesion in the presence of a liquid is reproduced in the appendix.

It was realised however that the original values for work of adhesion of the solid sealants in the presence of a liquid were based on carefully mixed sealant compositions. By taking the dispersive (τ^d) and polar (τ^p) components for

plasticiser (liquid) and polymer (adhesive) and using glass as the substrate the work of adhesion is calculated to be

$$1.58\ mJm^{-2}$$

This value would indicate a potential risk to adhesion if the plasticiser becomes a separated liquid.

14 CONCLUSIONS

A number of workers have examined weakening of joints with either water immersion or high humidity ageing. However most of the work involves non glass surfaces and there is little in the literature concerning polysulfides. Some work looking at durability (142,143,144,145,146) had indicated different test methods, whilst Comyn and Kinloch had examined the role of humidity (147,148). Other works referred to included those looking at sealant durability (149,150,151,152).

Some conference papers also proved useful as background data (153,154,155,156), as did articles by Garnish and Hanhella (157,158).

The selection of sealant formulations had been made to minimise the variations to those thought most likely to be associated with any joint weakening. The role of polymer and plasticiser were not known in respect of adhesion bond strength . The cure regime, and level of curative was kept constant , as was the type of filler used.

As mentioned in the results sections of chapters 7 and 8 no age hardening or shift in Tg was detected by either DMTA or DSC. Similarly the modulus above the Tg. remained constant, and therefore it is concluded that the weakening of joints cannot be attributed to any change in physical properties of the sealant. The stability of physical properties also showed

that cure was complete before testing commenced. This was important as undercure could have led to a false impression of adhesion characteristics due to a high level of stress relaxation of the sealant.

Also, although incompatibility had been noted at the higher levels of plasticiser incorporation in both the miscibility/compatibility test (see section 12) and adhesion test (see section 10), there was nothing in the DMTA or DSC traces to indicate onset of incompatibility.

The changes in Tg noted for the mixed compounds and for the unfilled systems indicated a level of non-solubility as it would be expected that the Tg would be lower for the plasticised systems than for the pure polymer. None of the traditional methods of examining plasticiser compatibility could be used to indicate potential problems, even the viscosity of the blends between 0 and 100 parts/ 100 rubber when plotted gave a smooth curve.

Taking the main items of investigation the following conclusions can be drawn:

The main conclusion from the mass uptake experiments is that the diffusion coefficient of the sealants were substantially independent of formulation. The level of weight loss after testing was also independent of formulation but could have been caused by carbon dioxide evolution from the filler reacting with acidic by-products within the sealant.

Mass uptake/water diffusion experiments indicate a relationship between water solubles in the curative and the diffusion coefficient. Therefore if there is a relationship between diffusion and adhesion this will be affected by the choice of curative. This could be demonstrated by a separate programme of work comparing totally soluble curatives, such as sodium perborate monohydrate, to the manganese dioxide used in this project.

The mass uptake of plasticiser in the sealant indicated a maximum level of incorporation of 55-60% above which little or no uptake was detected. This is in line with adhesion testing results in that those sealants with a plasticiser level above 60 phr showed rapid adhesion failure. It would appear that this technique could be used as a more accurate determination of the maximum level of plasticiser that can safely be incorporated in sealants than other methods so far considered in the sealant industry.

The adhesion testing showed that all systems developed some adhesion failure over time. The systems with the highest plasticiser content failed immediately, this failure being due to plasticiser migration to the sealant/glass interface.The appearance of a discoloured boundary layer was interesting, and the rate of growth of the boundary layer matched that of the increase of adhesion failure.

The various types of adhesion failure were described in the introduction to thermodynamics of adhesion, section 14, as being a) weak boundary layer

b) surface roughness and c) diffusion. The surface roughness effect is not considered here as the surface for all tests was glass and therefore variations could not be studied.

The weak boundary layer process was considered and this appears to be a real effect as the bond strength reduces with time in the test chamber and the mode of failure changes from true cohesive to adhesive via an apparent weakening at the interface. Over the earlier periods of ageing (1-6 months) the rate of increase in the level of adhesion failure increases with the level of plasticiser incorporation. Thus the mechanism of failure involves three stages , all of which are diffusion controlled.

During the ageing period the concentration of water increases in the sealant causing a lowering of the modulus. As diffusion coefficients, for water, of the sealants tested were independent of formulation, this in itself is not a primary cause of failure.

The increase in water concentration causes plasticiser migration to the interface , and this together with the water plasticisation produces a weak boundary layer. This process is related to the plasticiser concentration in the formulation.

Finally the combination of plasticiser and water creates the conditions of adhesion failure. Once failure had occurred, water could penetrate between

the sealant and the glass destroying any possibility of bond recovery when the sealant dries out.

The above process explains why, even with joints showing cohesive failure, the loci of failure move towards the interface with increasing ageing periods.

The surface analysis of the failed interface supported the view expressed above in that the levels of organic oxygen increased as the bond tended towards adhesion failure. Also the levels of sulfur diminished indicating an increase in plasticiser at the interface.

From the plasticiser mass uptake experiments there is a maximum level of plasticiser of 60 parts by weight to 100 parts of polymer above which little plasticiser could diffuse into the sealant. This leads to the conclusion that above that level a more mobile diffusant would displace the plasticiser, this argument was strengthened by the fact that within these experiments, sealants with a high plasticiser level showed adhesive failure more rapidly than the lower incorporation levels.

Thermodynamic considerations also support the above view in that the work of adhesion in the presence of water, and in the presence of plasticiser is zero or negative. The work of adhesion in the presence of plasticiser is slightly worse than that with water , and thus becomes the predominant factor in the adhesion failure process.

Thus the formulator has the provision for increasing the adhesion life expectancy of his sealant by a) selecting a curative that has a low cold water solubility content and b) selecting a good plasticiser and c) selecting a level of plasticiser that is high enough to give the desired physical properties, but not so high as to give adhesion failure should the joint be subjected to moisture when in service. The level of plasticiser can be determined from mass uptake experiments.

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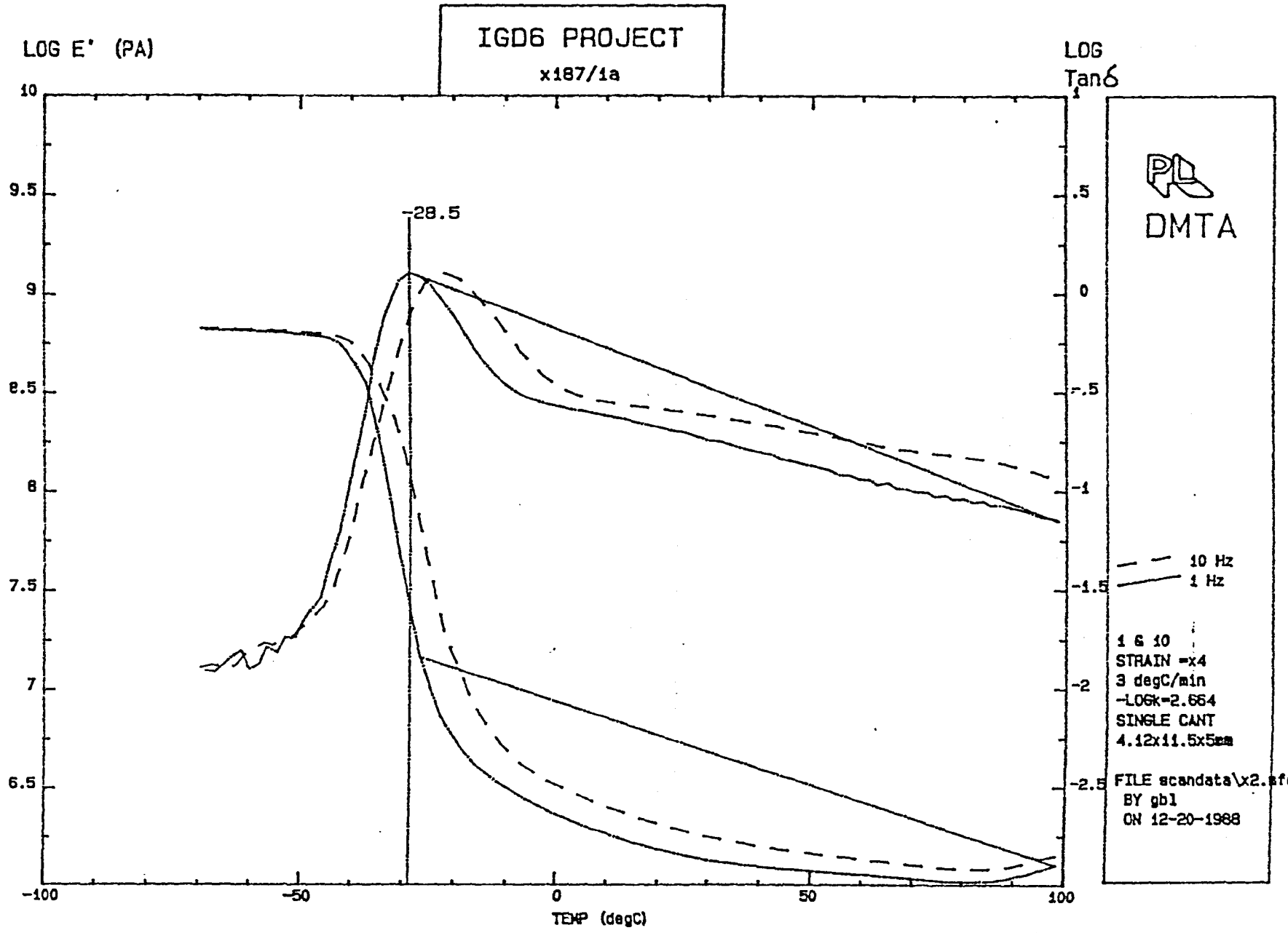
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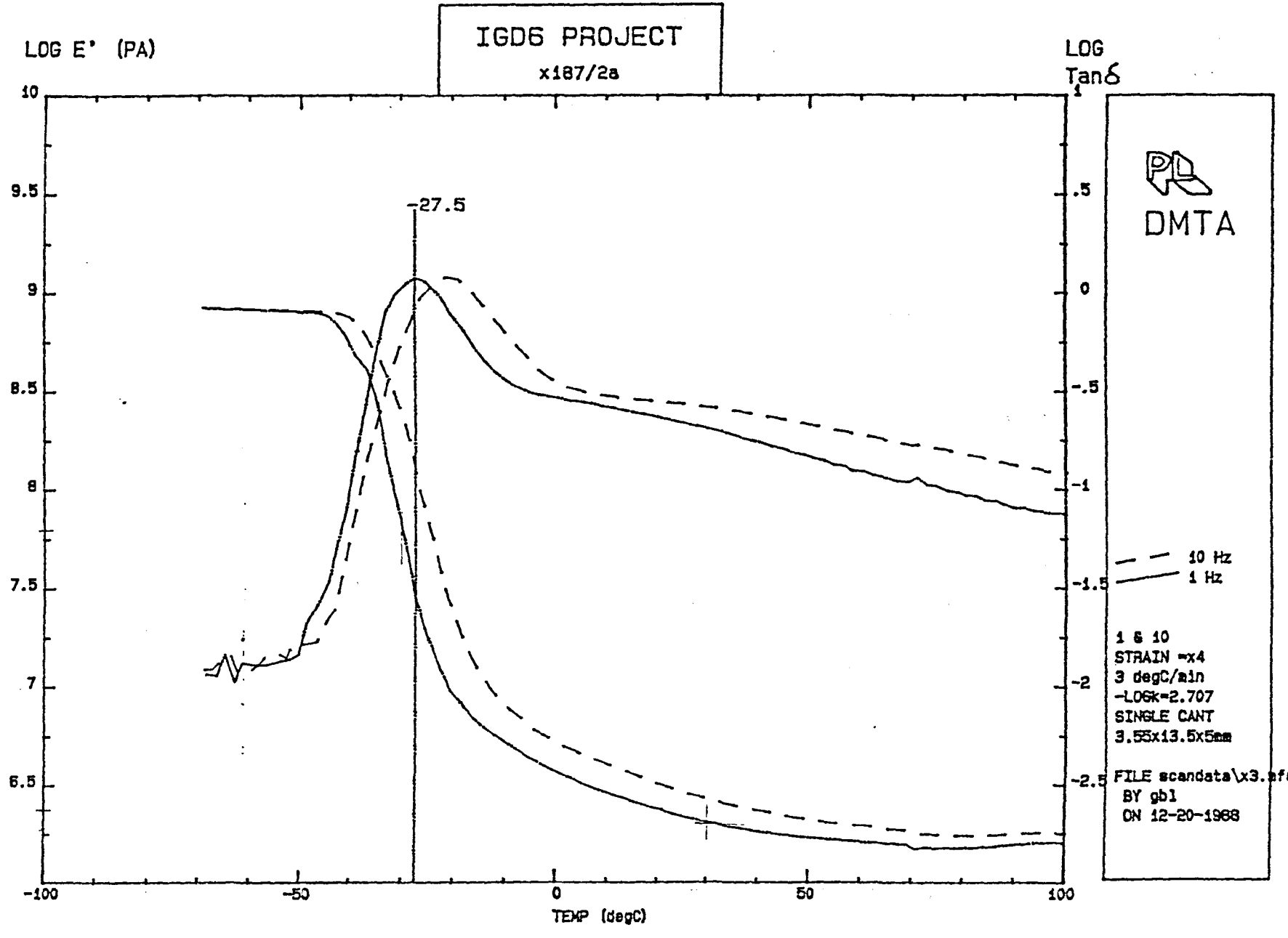
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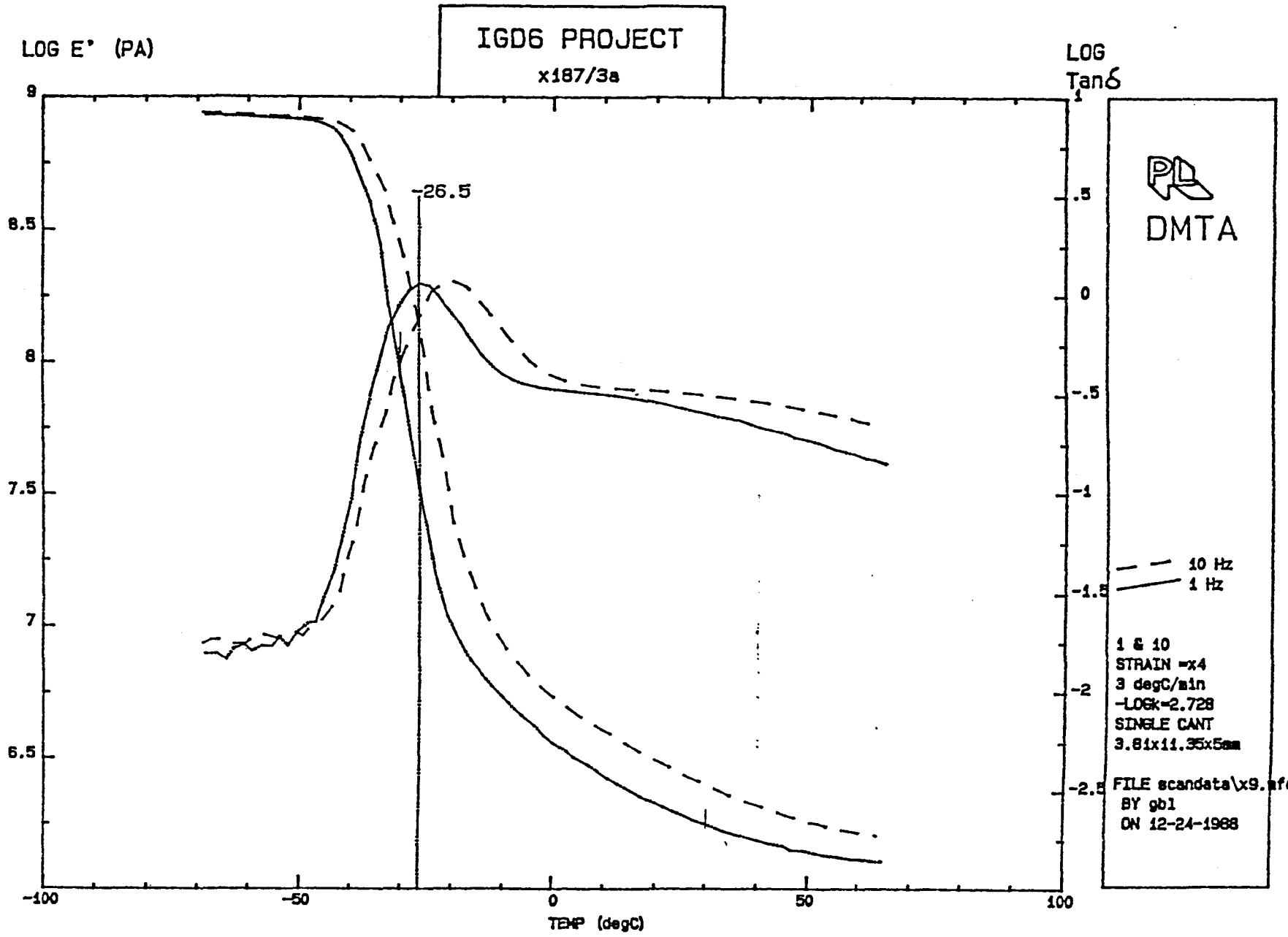
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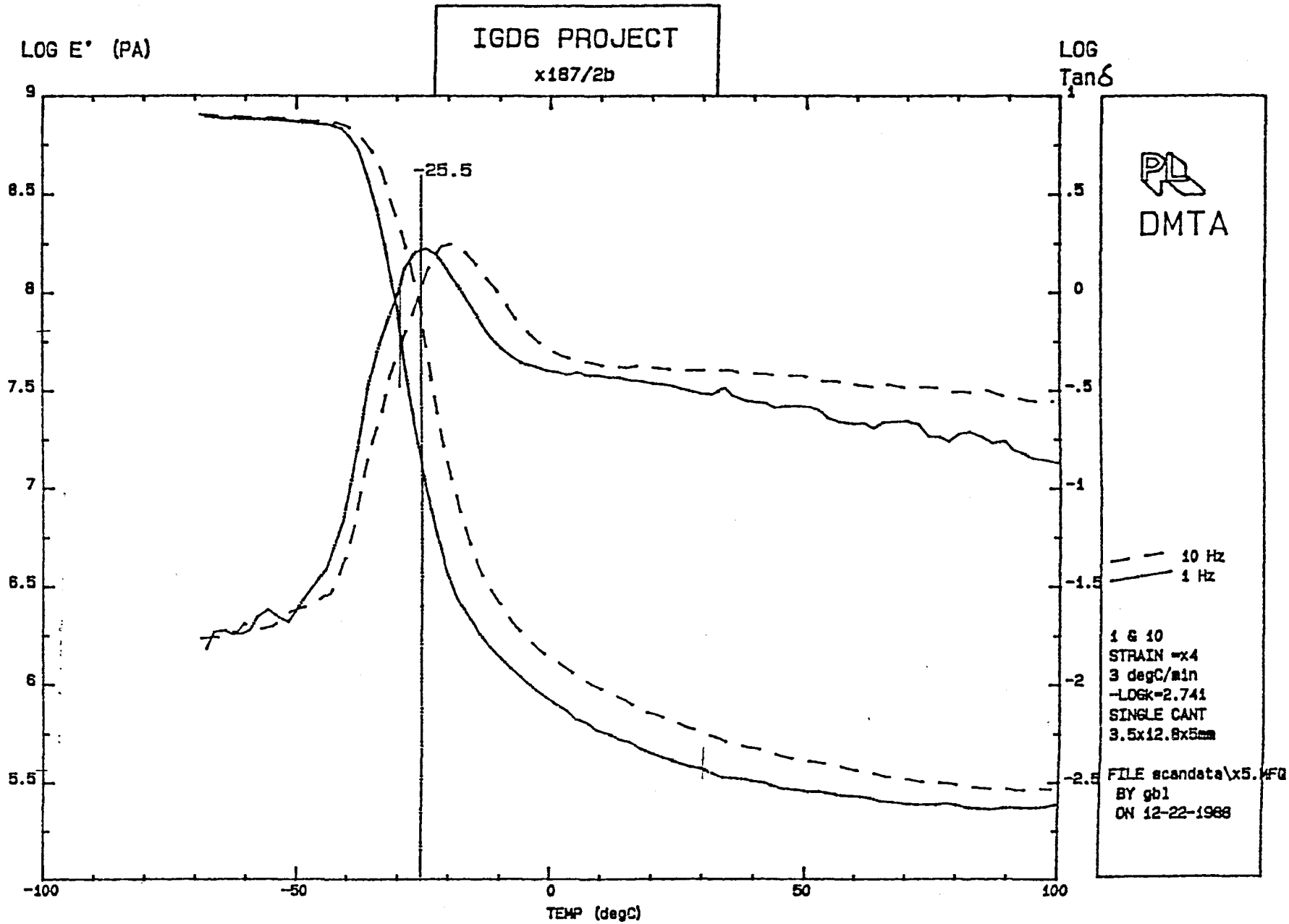
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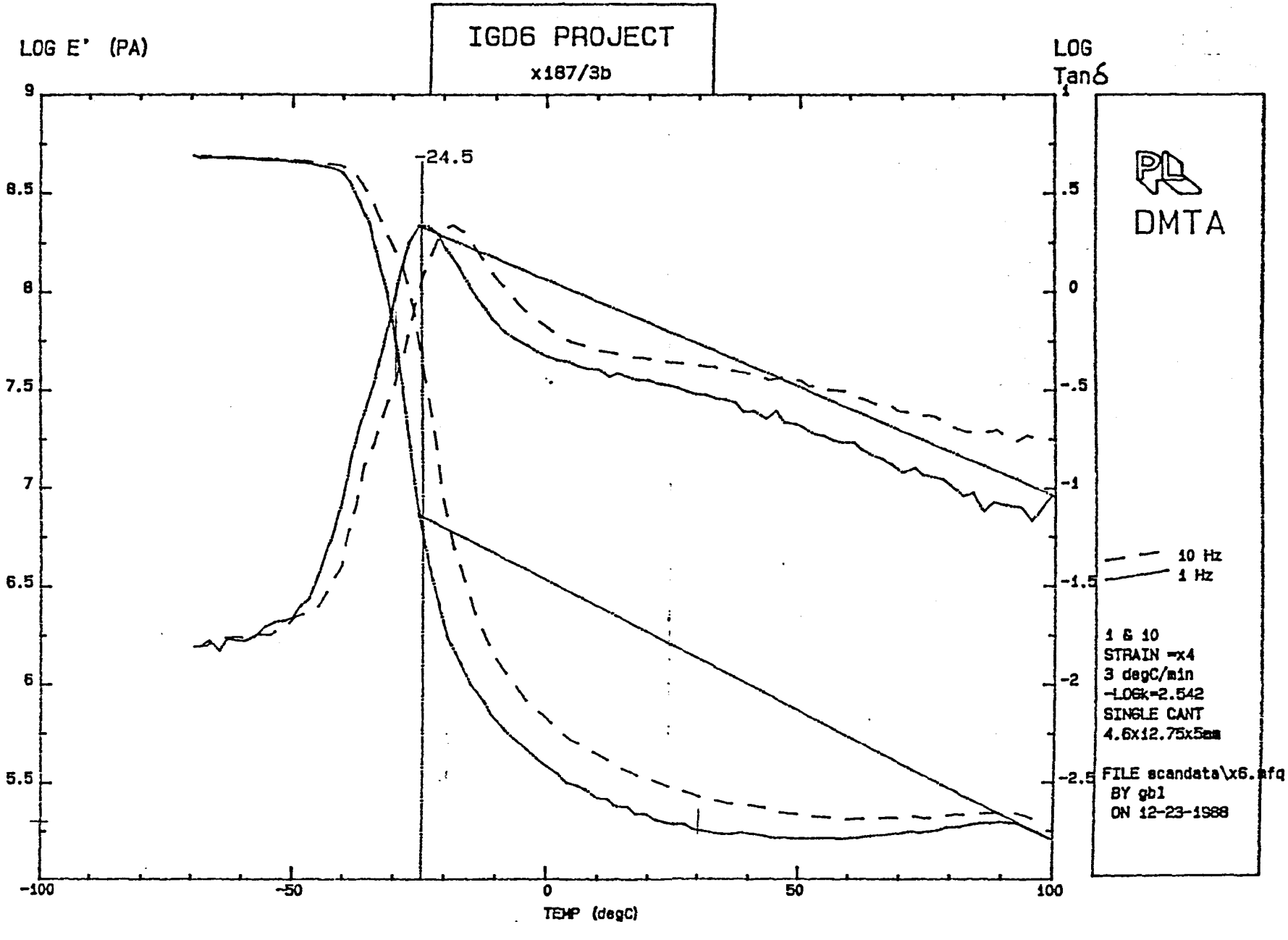
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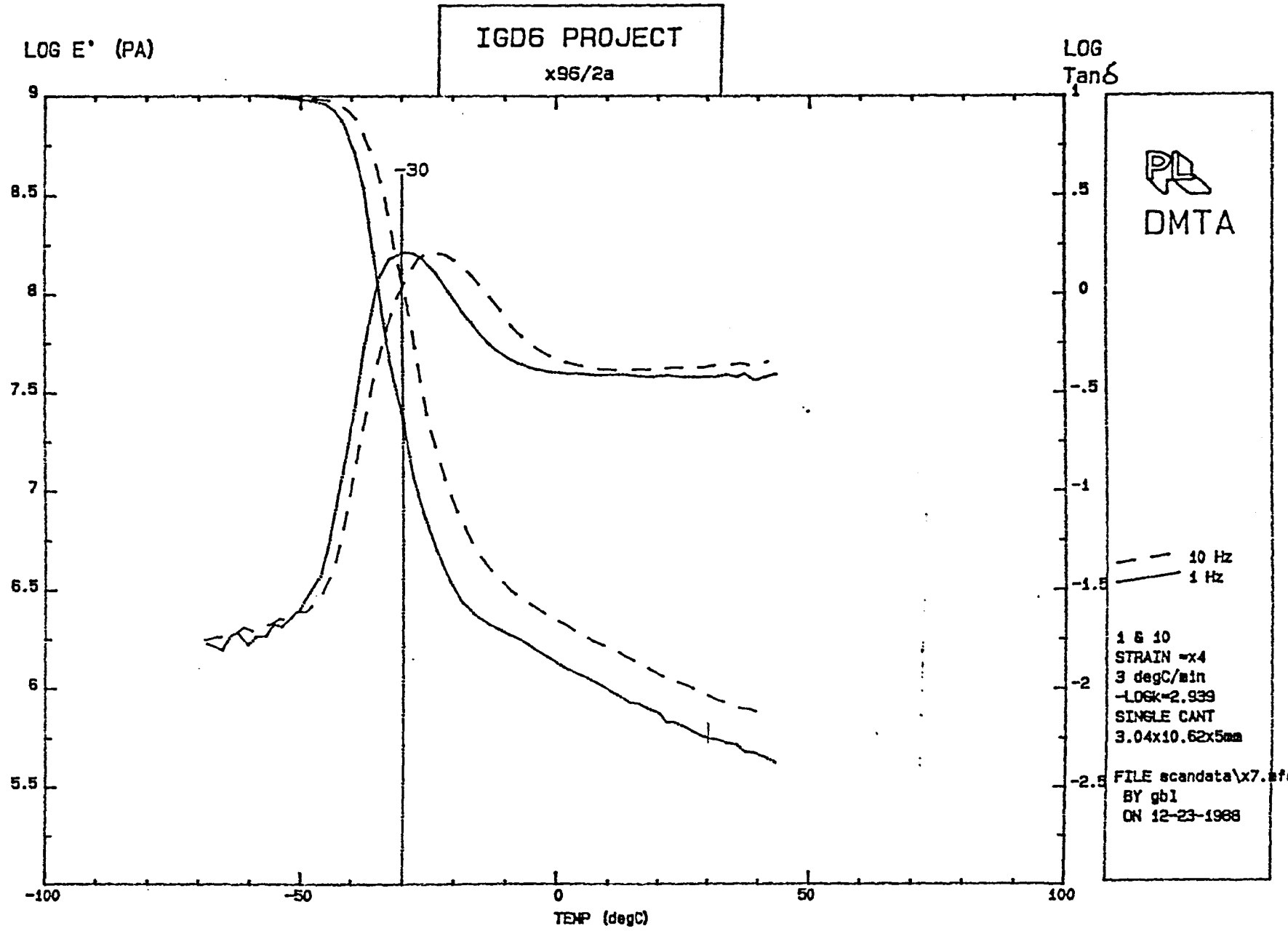
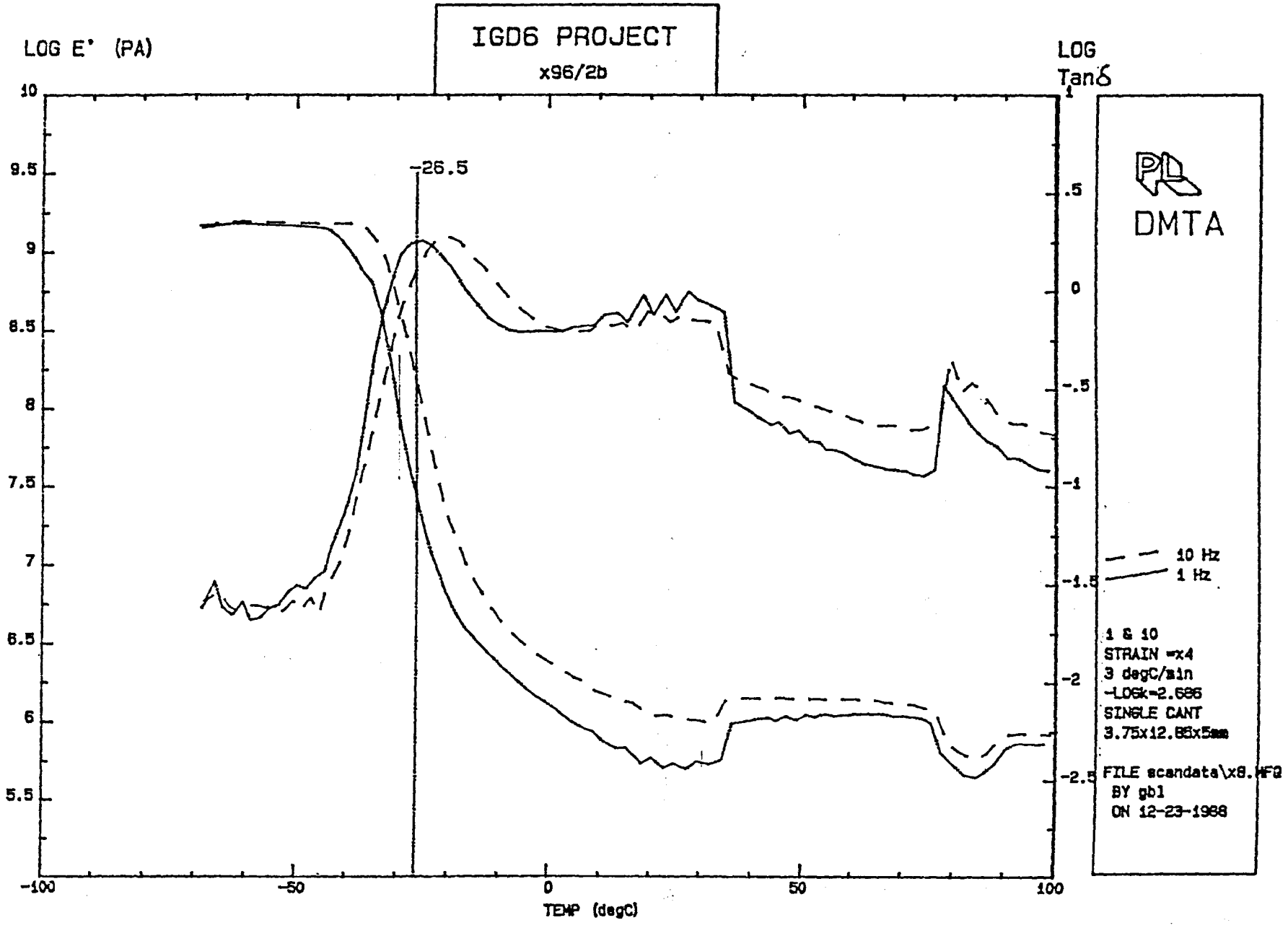
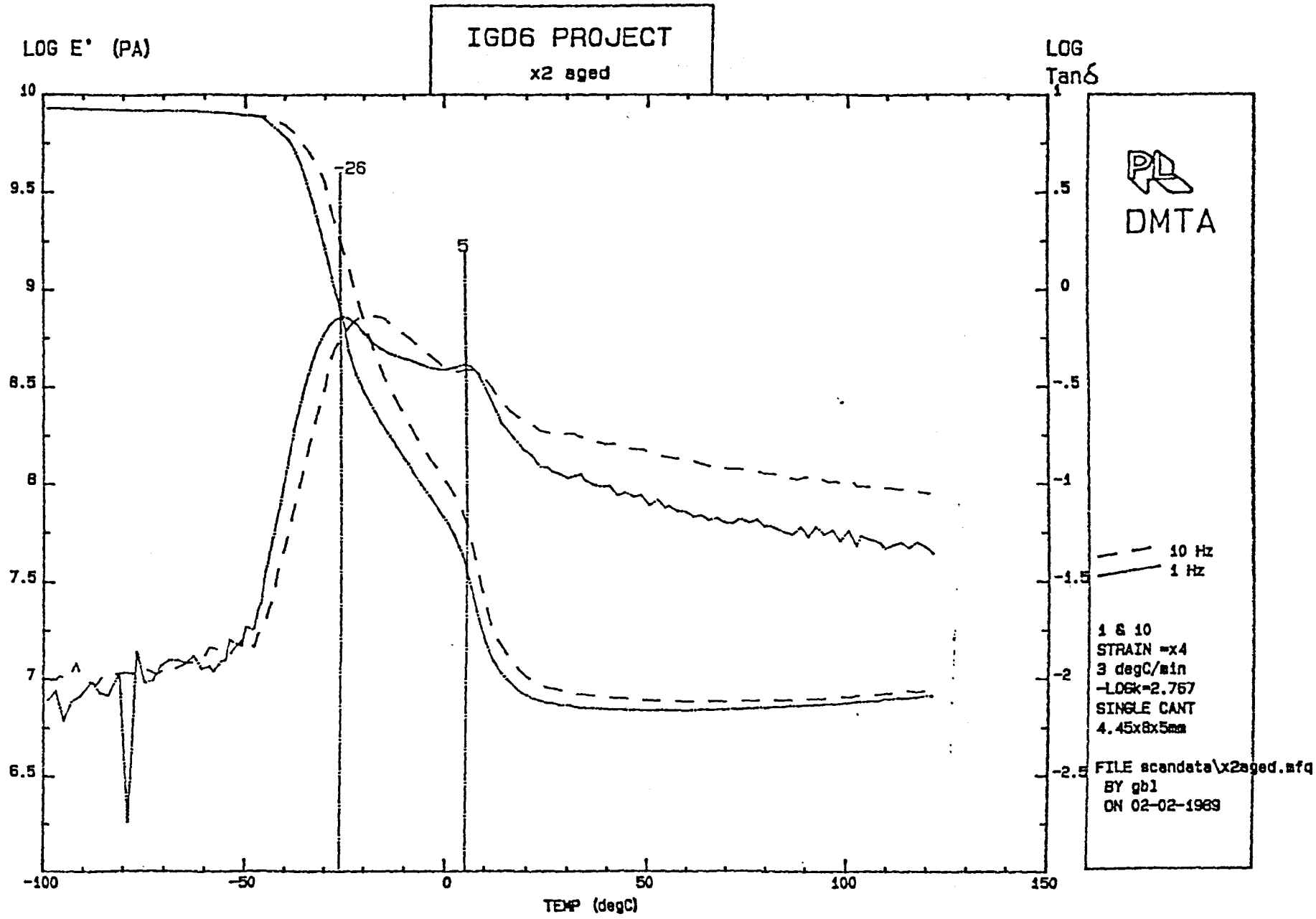
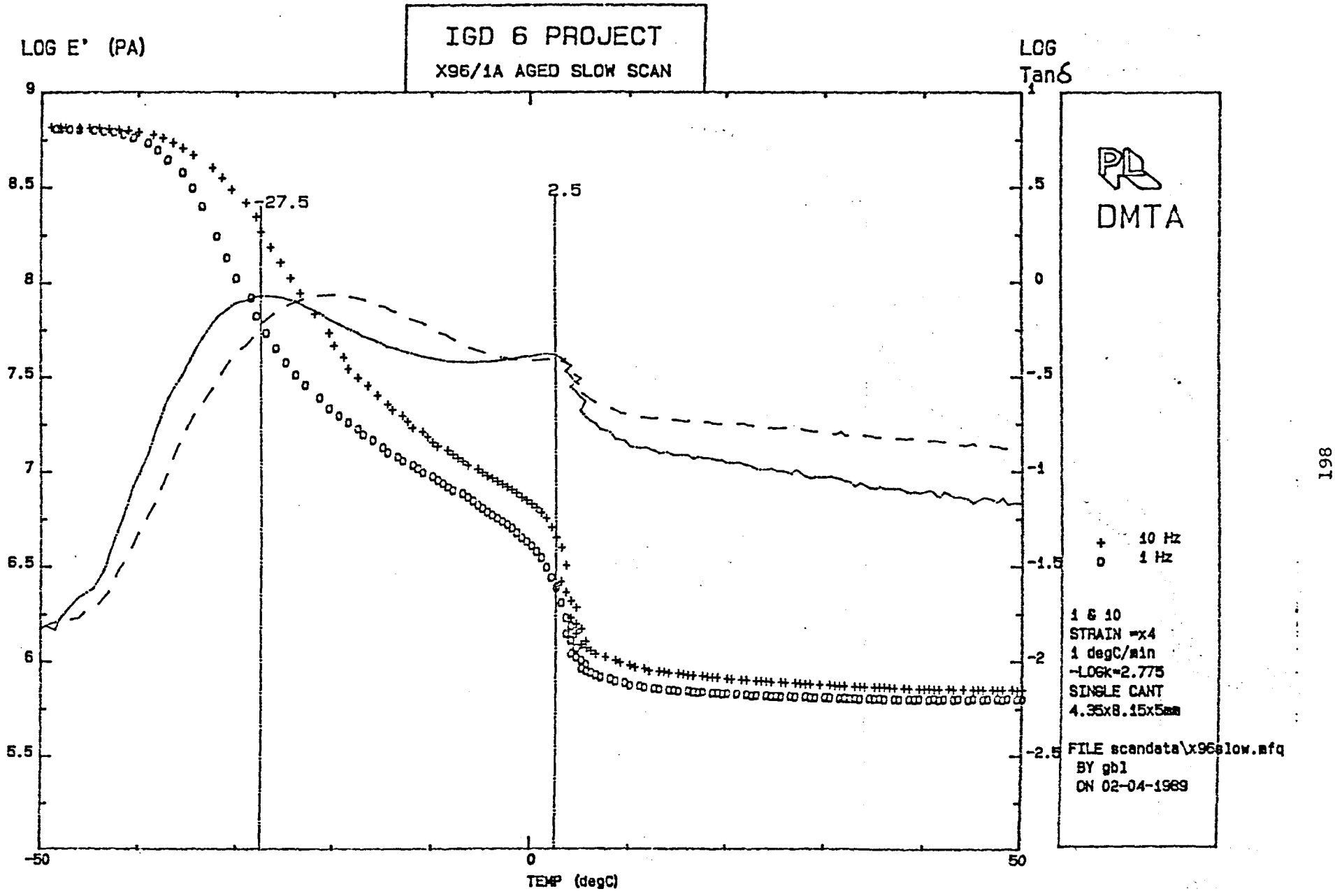
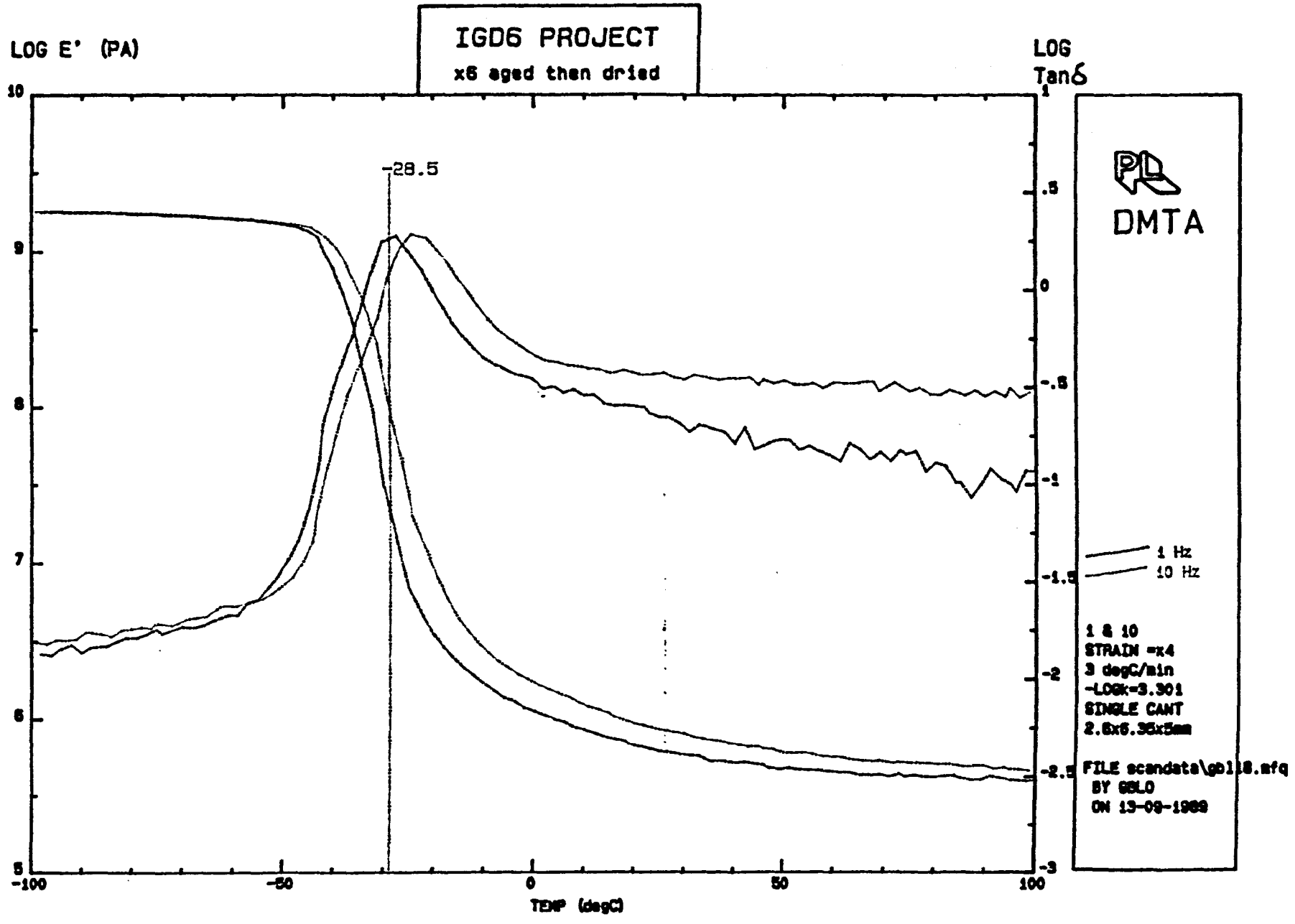
STRAIN =x4
3 degC/min
-LOGk=2.542
SINGLE CANT
4.6x12.75x5mm
FILE scandata\x6.dfq
BY gbl
ON 12-23-1988

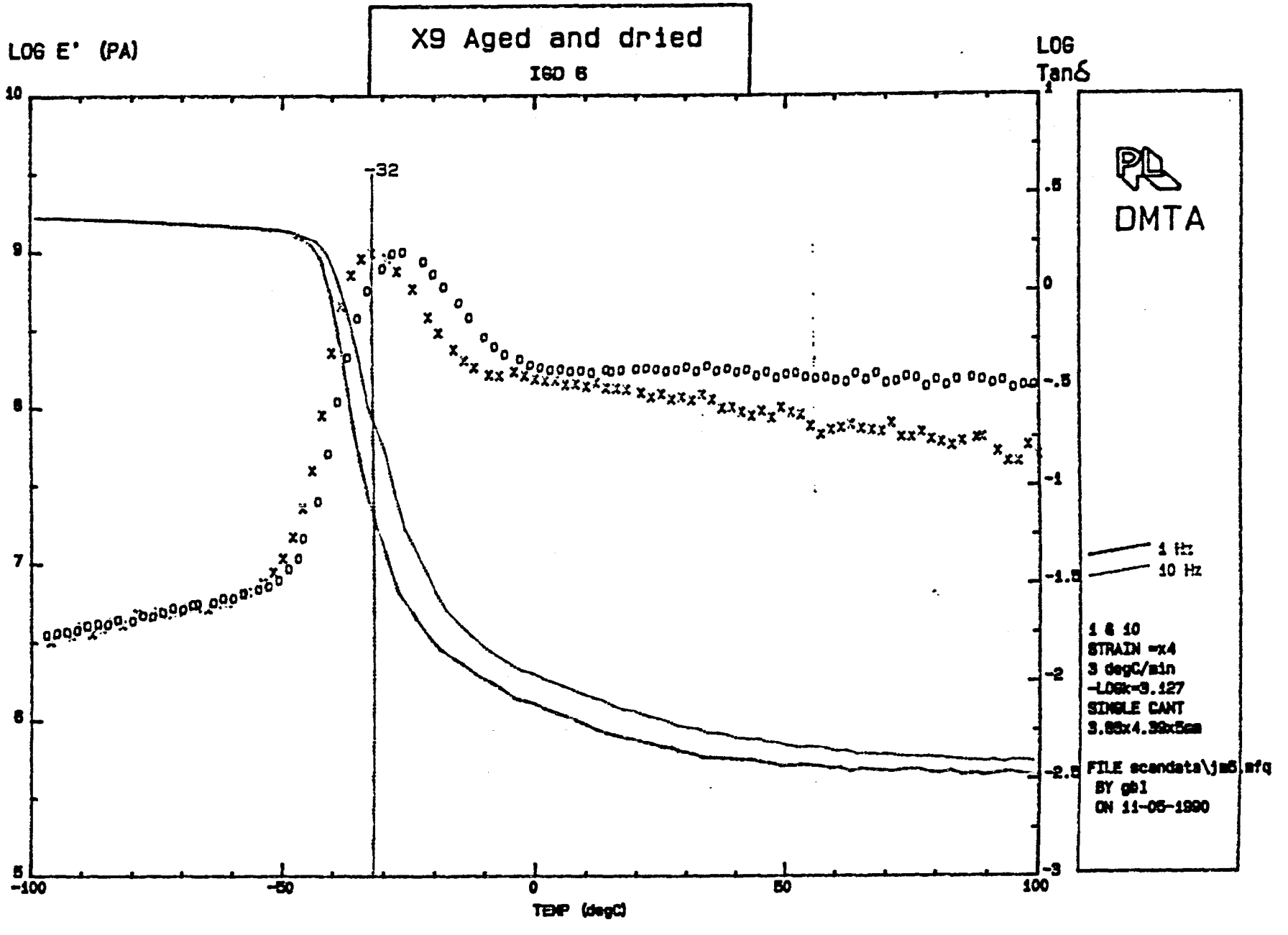

IGD6 PROJECT
x96/2a
LOG E' (PA)
LOG Tanδ
9
8.5
8
7.5
7
6.5
6
5.5
1
.5
0
-.5
-1
-1.5
-2
-2.5
-30
-100
-50
0
50
100
TEMP (degC)
PL
DMTA
10 Hz
1 Hz
1 & 10
STRAIN =x4
3 degC/min
-LOGK=2.939
SINGLE CANT
3.04x10.62x5mm
FILE scandata\x7.dfq
BY gbl
ON 12-23-1988

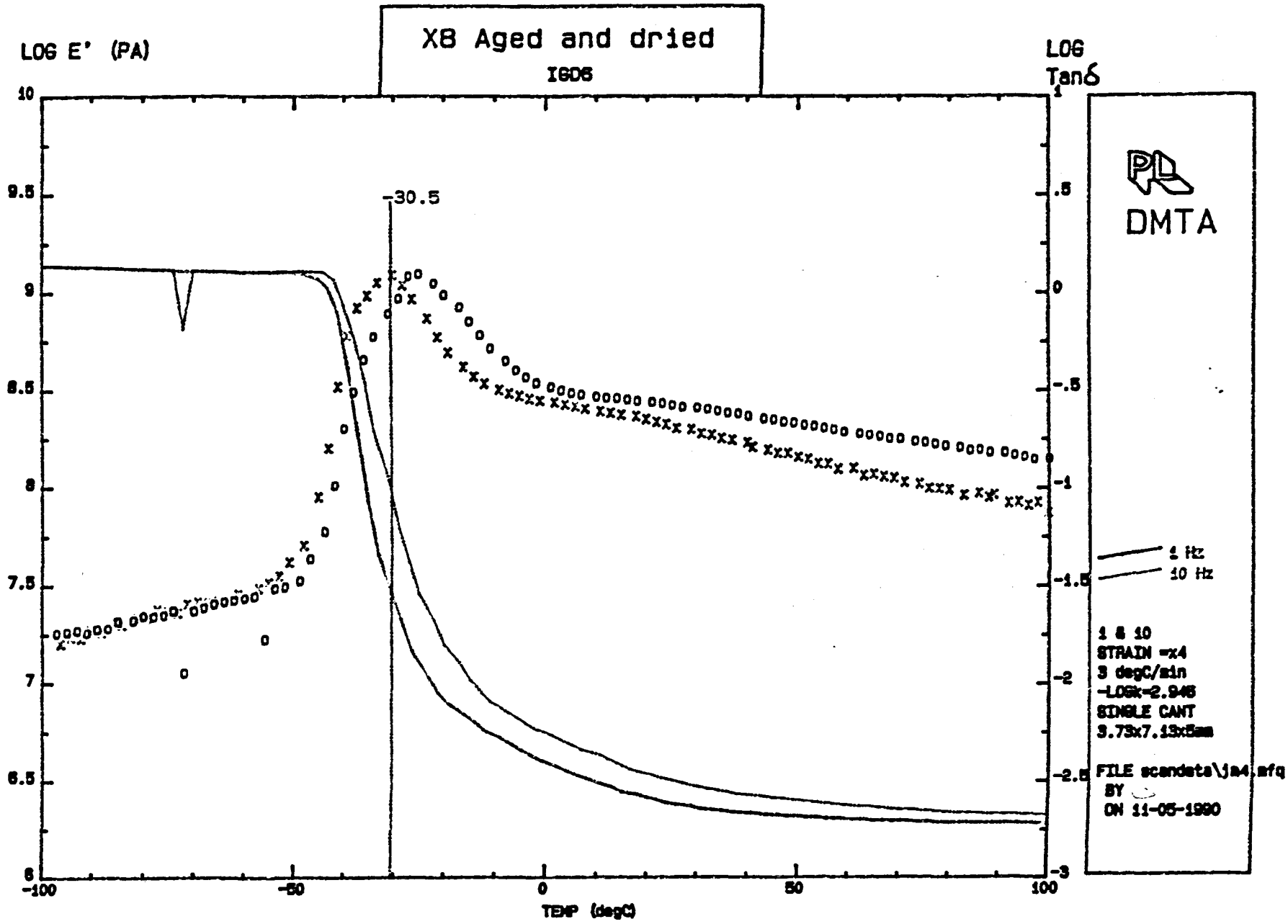

IGD6 PROJECT
x96/2b
LOG E' (PA)
LOG Tanδ
-26.5
DMTA
10 Hz
1 Hz
1 & 10
STRAIN =x4
3 degC/min
-LOGk=2.686
SINGLE CANT
3.75x12.85x5mm
FILE scandata\x8.MFA
BY gbl
ON 12-23-1988
TEMP (degC)

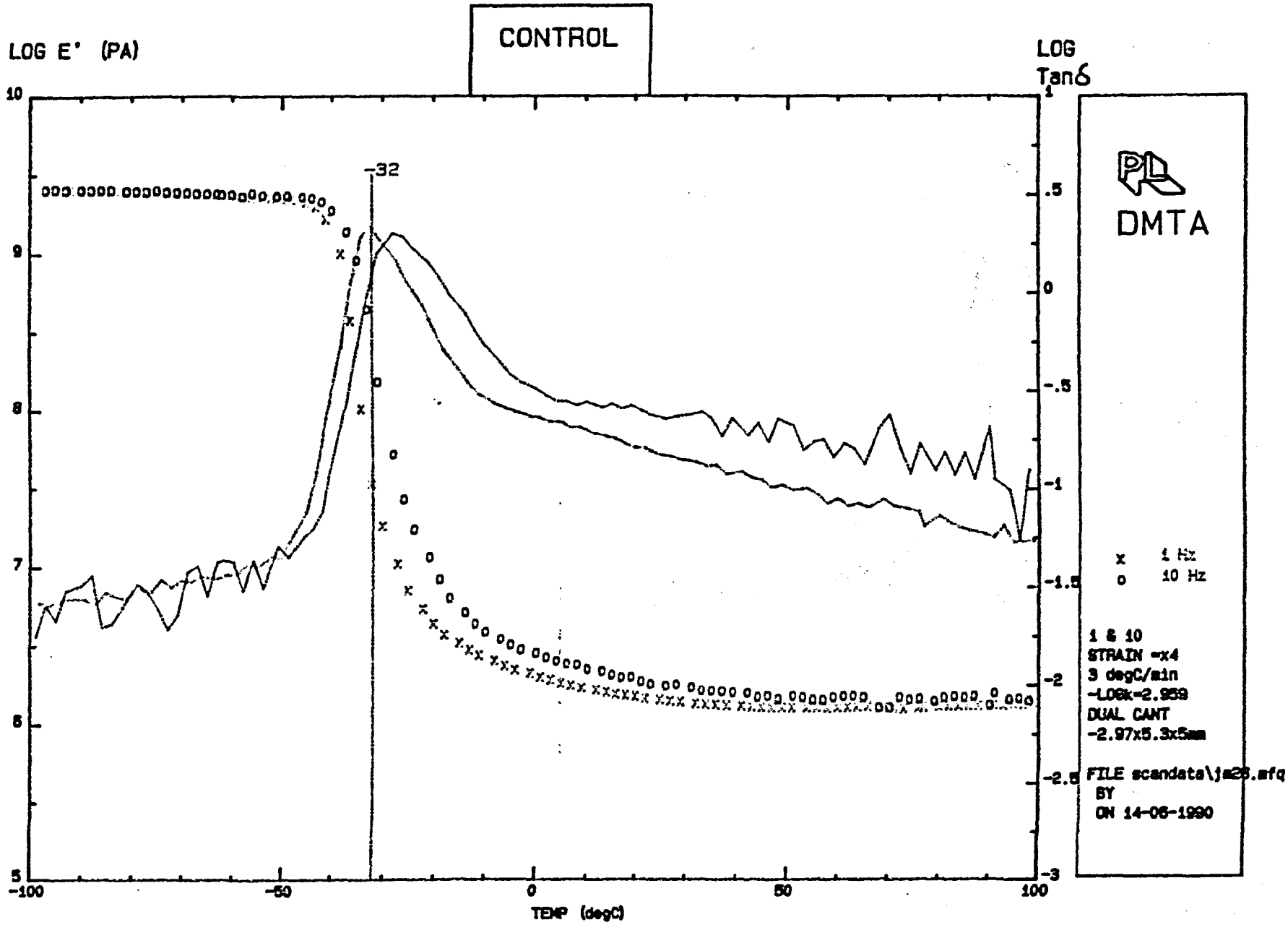

IGD6 PROJECT
x2 aged
LOG E' (PA)
LOG
Tanδ
10
9.5
9
8.5
8
7.5
7
6.5
1
.5
0
-.5
-1
-1.5
-2
-2.5
-26
5
-100
-50
0
50
100
150
TEMP (degC)
DMTA
10 Hz
1 Hz
1 & 10
STRAIN =x4
3 degC/min
-LOGk=2.767
SINGLE CANT
4.45x8x5mm
FILE scandata\x2aged.mfq
BY gbl
ON 02-02-1989

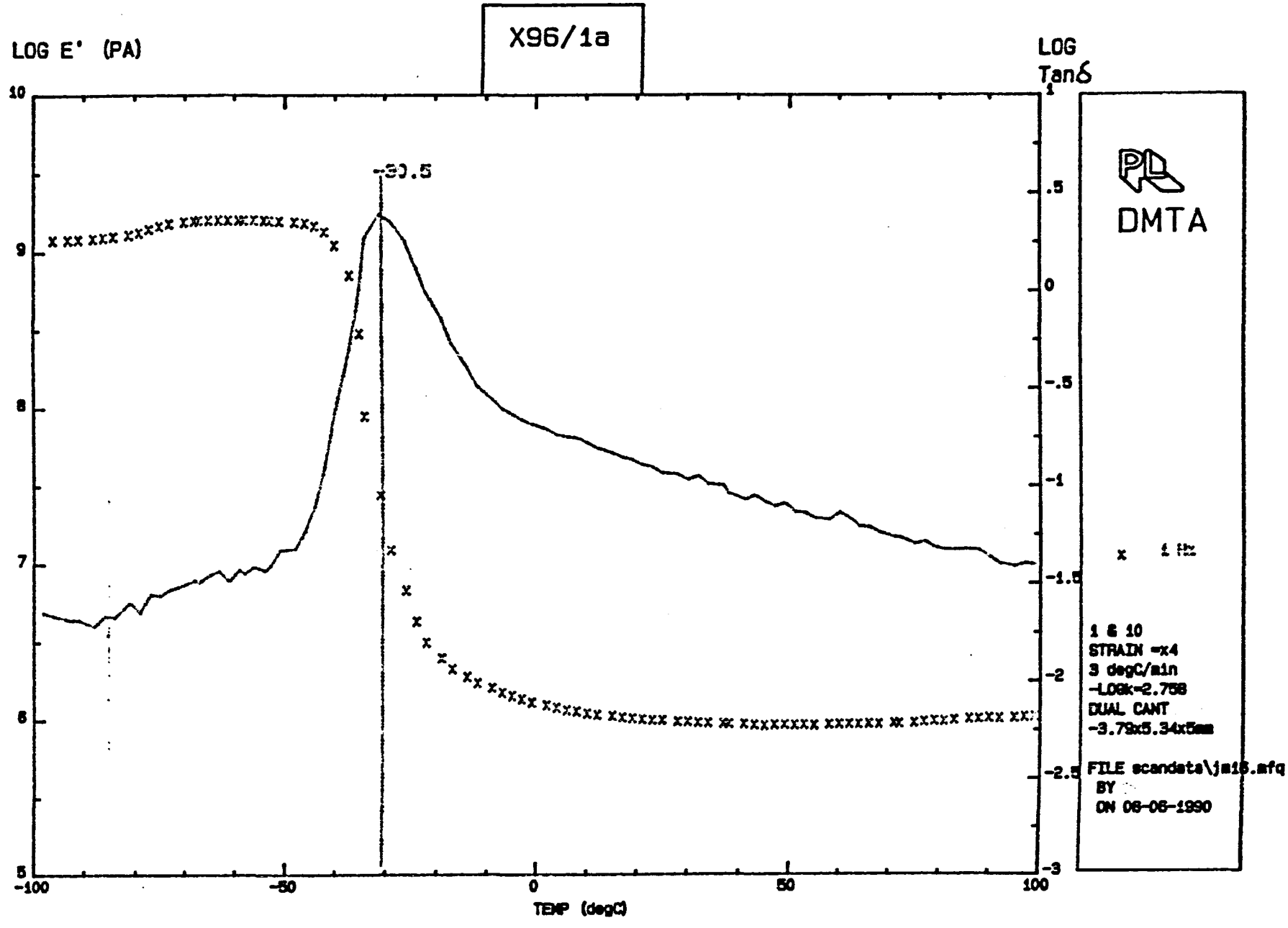

IGD 6 PROJECT
X96/1A AGED SLOW SCAN
LOG E' (PA)
LOG Tanδ
9
8.5
8
7.5
7
6.5
6
5.5
1
.5
0
-.5
-1
-1.5
-2
-2.5
-27.5
2.5
-50
0
50
TEMP (degC)
DMTA
+ 10 Hz
o 1 Hz
1 & 10
STRAIN =x4
1 degC/min
-LOGK=2.775
SINGLE CANT
4.35x8.15x5mm
FILE scandata\x96slow.mfq
BY gbl
ON 02-04-1989

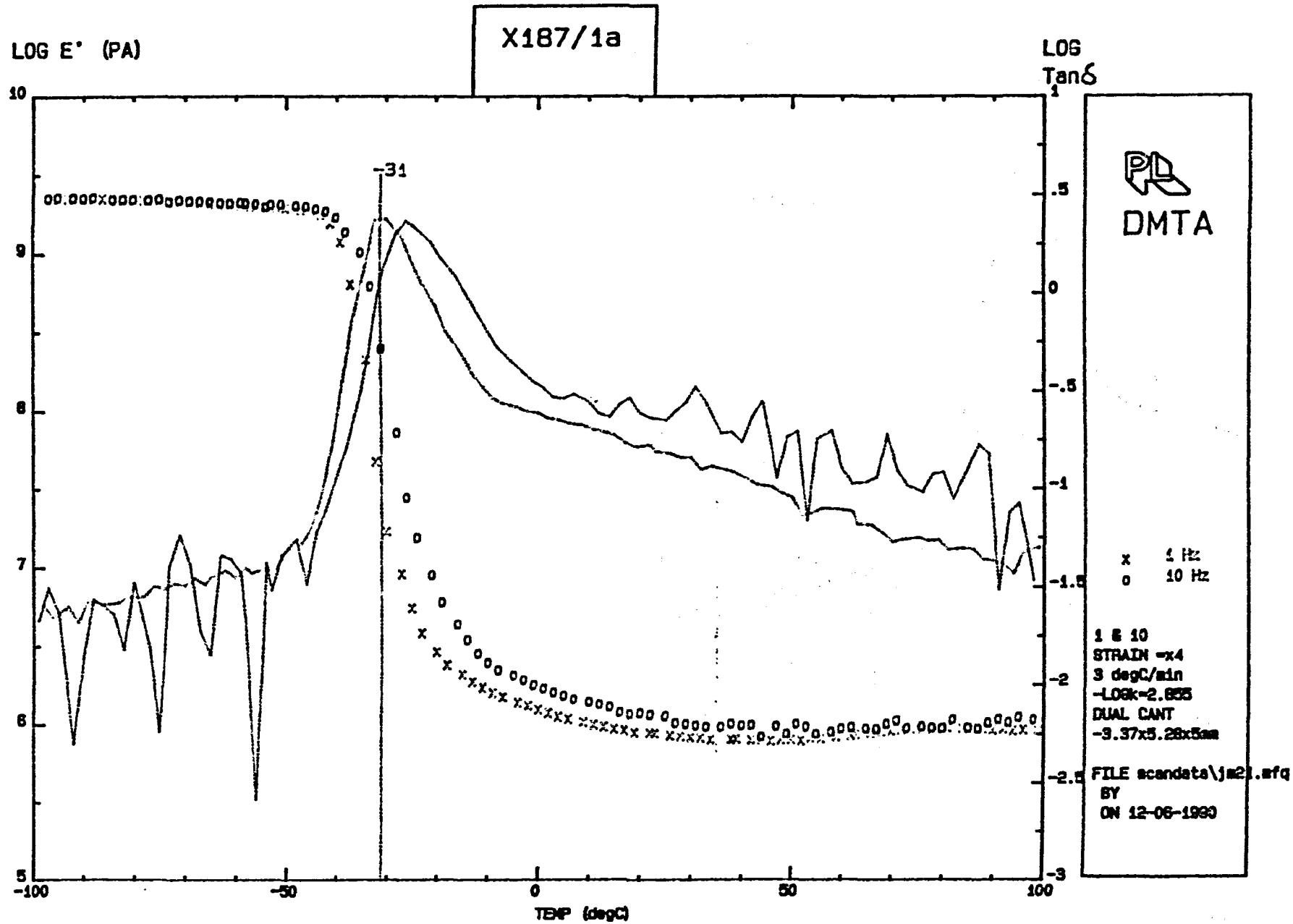

IGD6 PROJECT
x6 aged then dried
LOG E' (PA)
LOG Tanδ
-28.5
DMTA
1 Hz
10 Hz
1 & 10
STRAIN =x4
3 degC/min
-LOGK=3.301
SINGLE CANT
2.6x6.36x5mm
FILE scandata\gb118.mfq
BY GBLO
ON 13-09-1989
TEMP (degC)

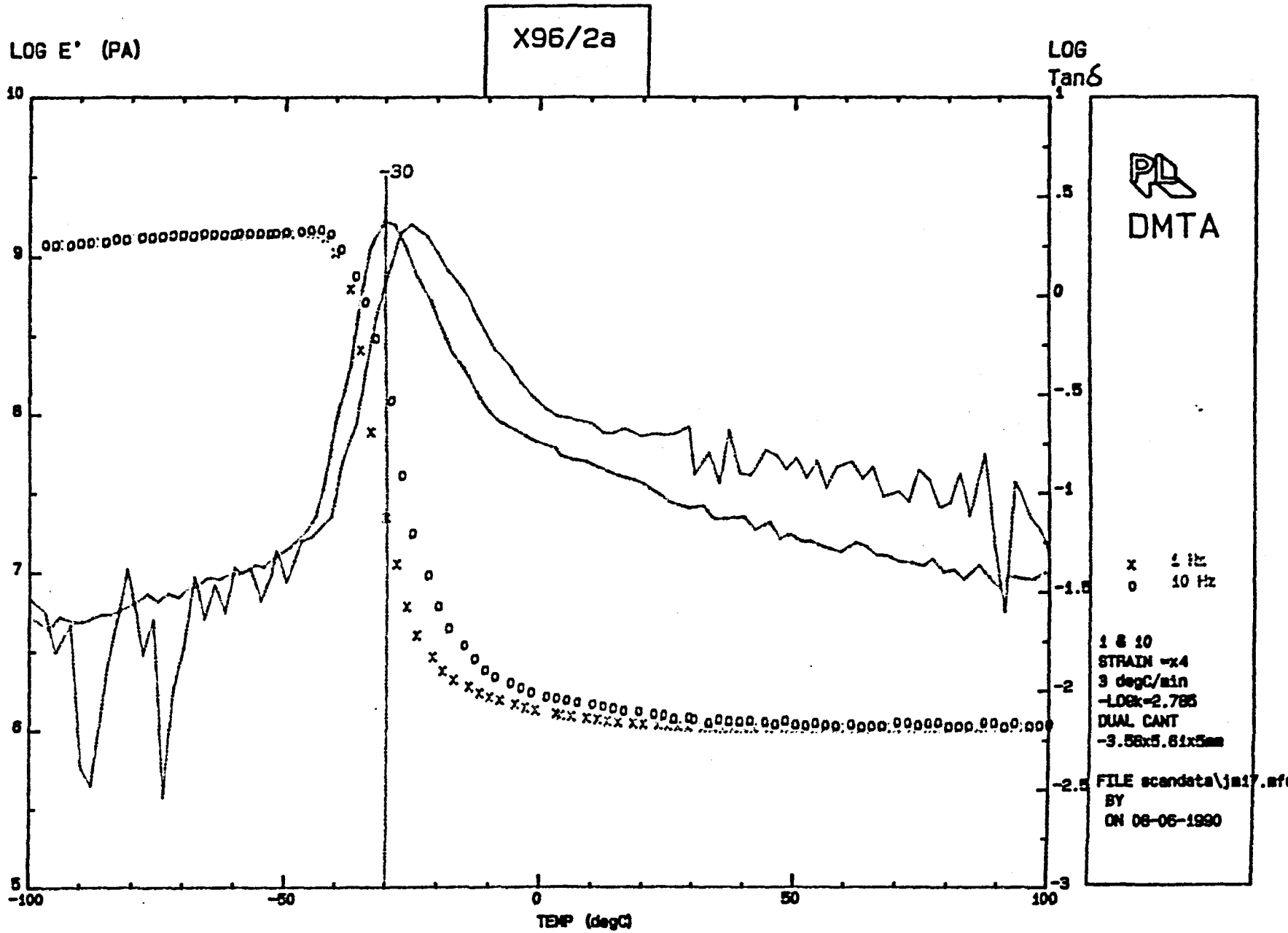

X9 Aged and dried
IGD 6
LOG E' (PA)
LOG Tanδ
-32
DMTA
1 Hz
10 Hz
1 & 10
STRAIN =x4
3 degC/min
-LOGK-9.127
SINGLE CANT
3.88x4.39x5cm
FILE scandata\jm6.mfq
BY gbl
ON 11-05-1990
TEMP (degC)
10
9
8
7
6
5
-100
-50
0
50
100
.5
0
-.5
-1
-1.5
-2
-2.5
-3

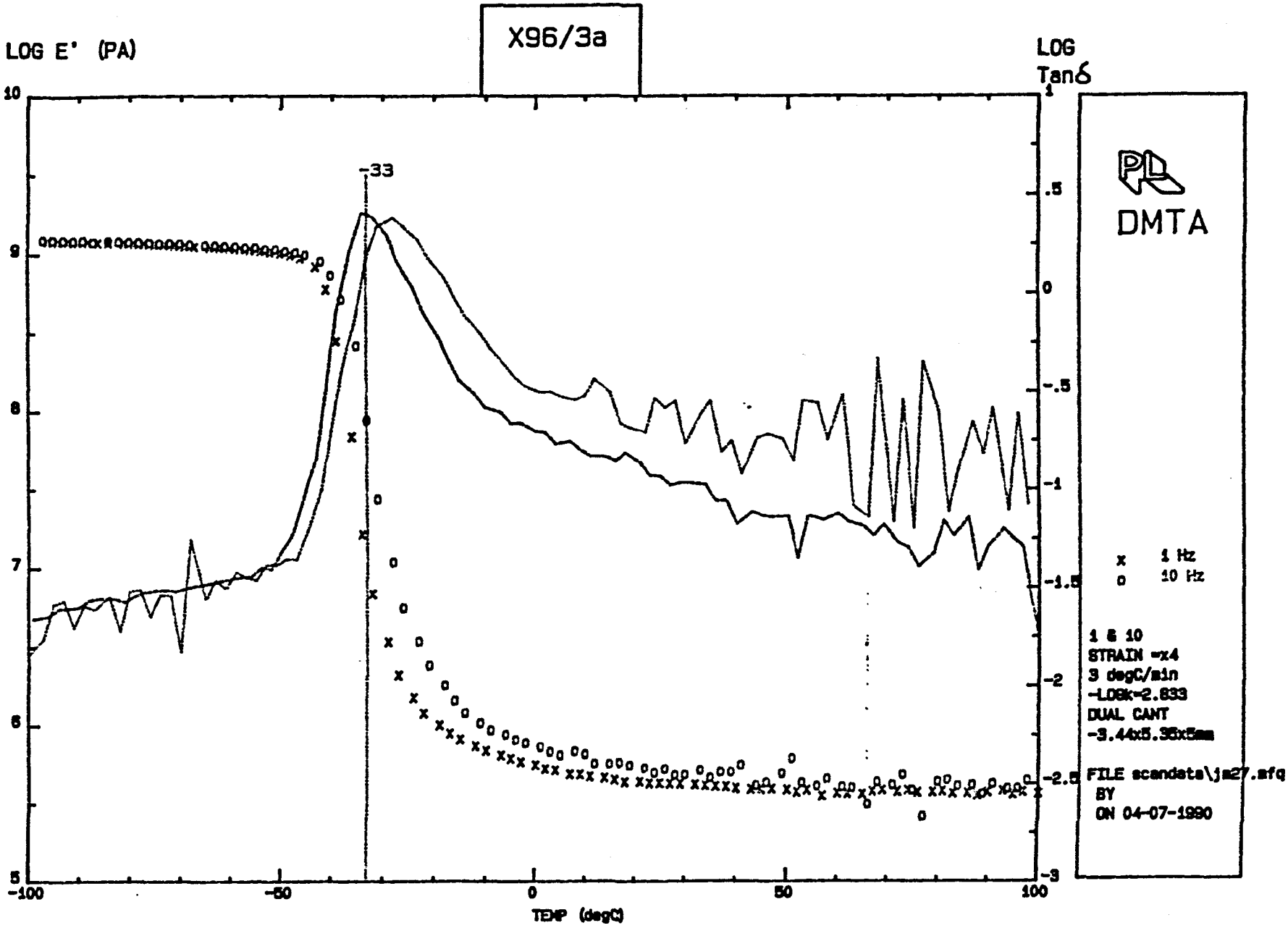

X8 Aged and dried
IGD6
LOG E' (PA)
LOG Tanδ
-30.5
DMTA
1 Hz
10 Hz
1 & 10
STRAIN =x4
3 degC/min
-LOGk=2.946
SINGLE CANT
3.73x7.13x5mm
FILE scandata\ja4.mfq
BY
ON 11-05-1990
TEMP (degC)

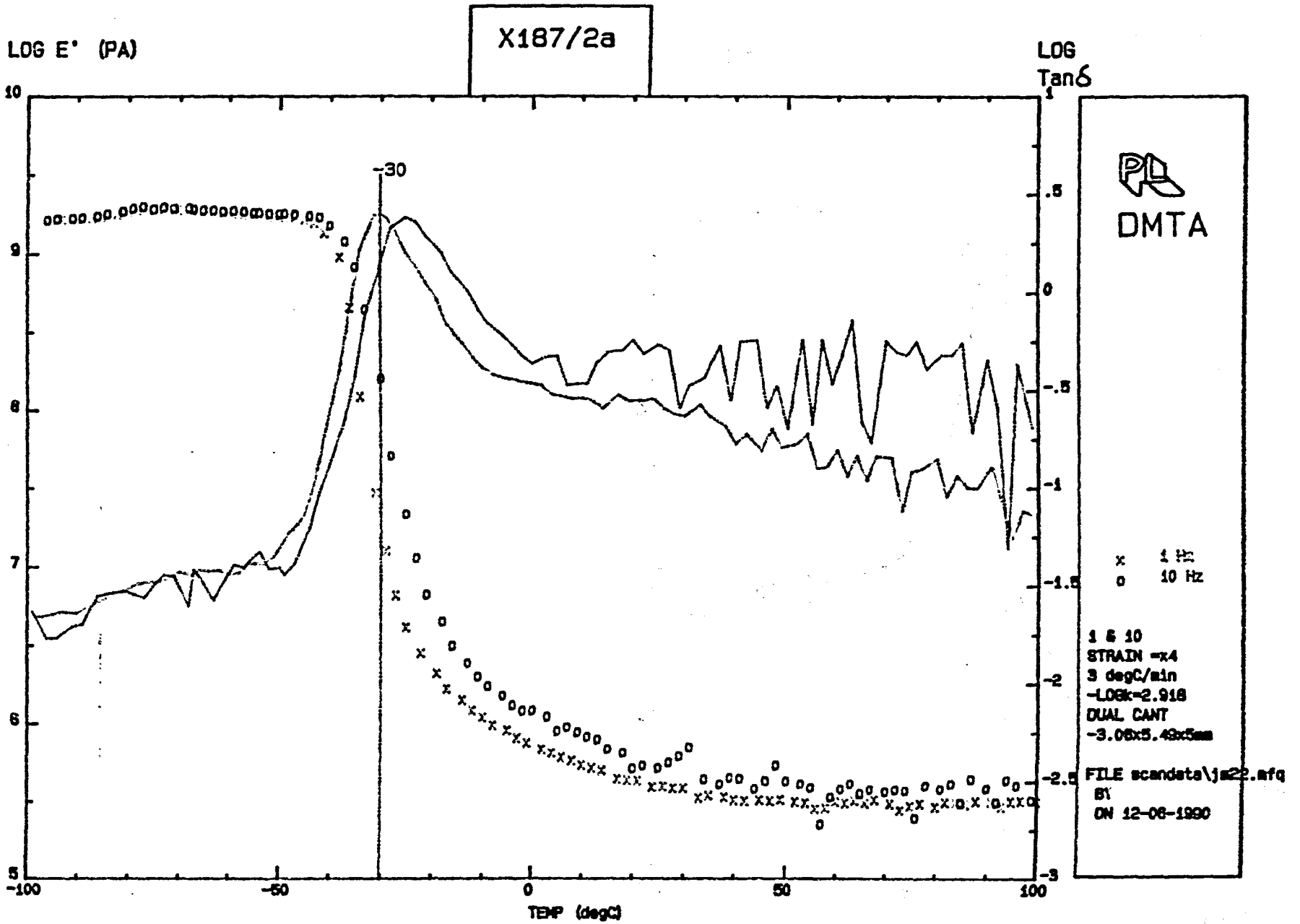

CONTROL
LOG E' (PA)
LOG Tanδ
10
9
8
7
6
5
1
.5
0
-.5
-1
-1.5
-2
-2.5
-3
-32
-100
-50
0
50
100
TEMP (degC)
DMTA
x 1 Hz
o 10 Hz
1 & 10
STRAIN =x4
3 degC/min
-LOGk=2.959
DUAL CANT
-2.97x5.3x5mm
FILE scandata\js26.mfq
BY
ON 14-06-1990

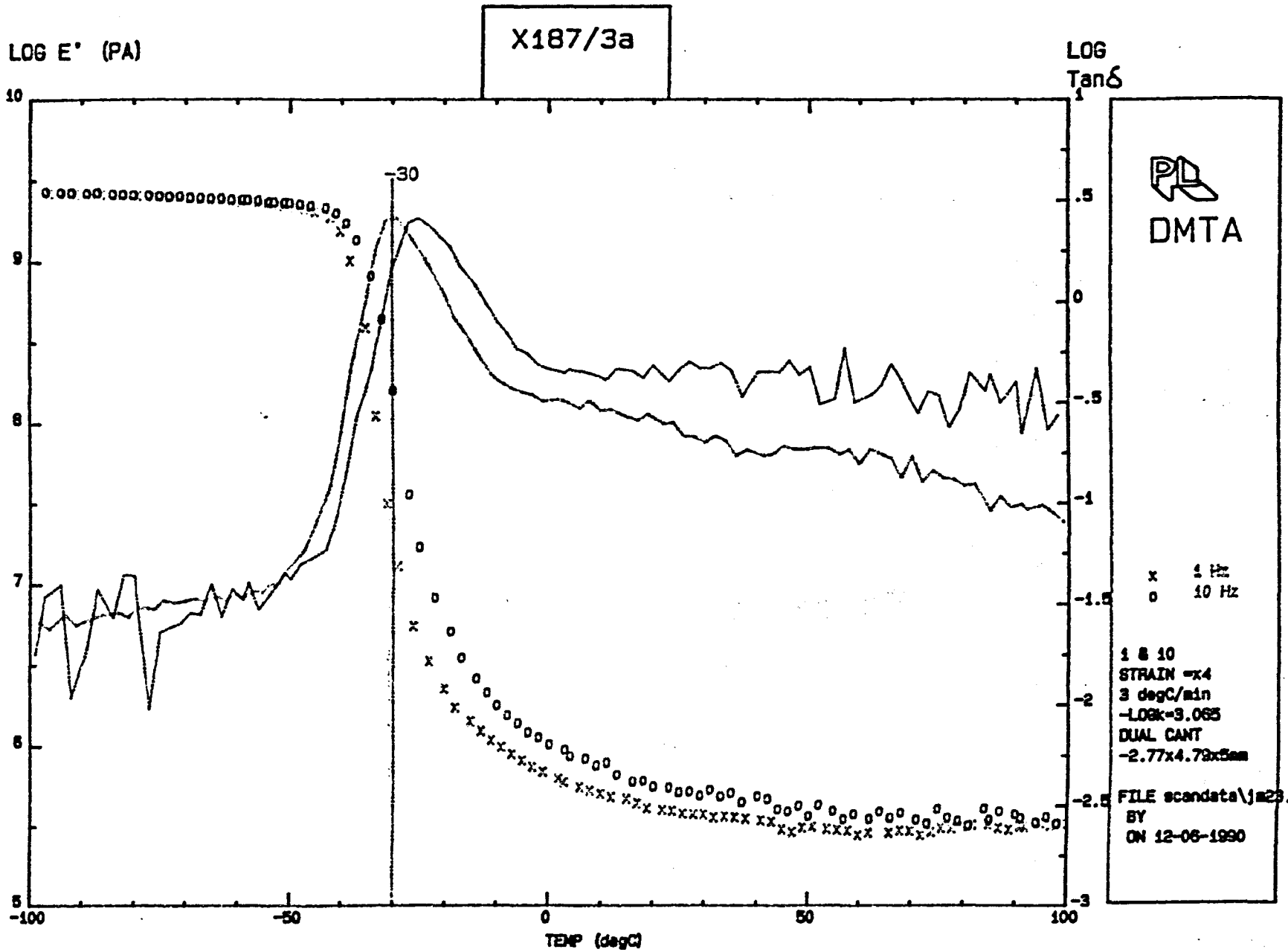

X96/1a
LOG E' (PA)
LOG Tanδ
-30.5
DMTA
1 & 10
STRAIN =x4
3 degC/min
-LOGk=2.758
DUAL CANT
-3.79x5.34x5mm
FILE scandata\jm16.mfq
BY
ON 06-06-1990
TEMP (degC)
10
9
8
7
6
5
1
.5
0
-.5
-1
-1.5
-2
-2.5
-3
-100
-50
0
50
100

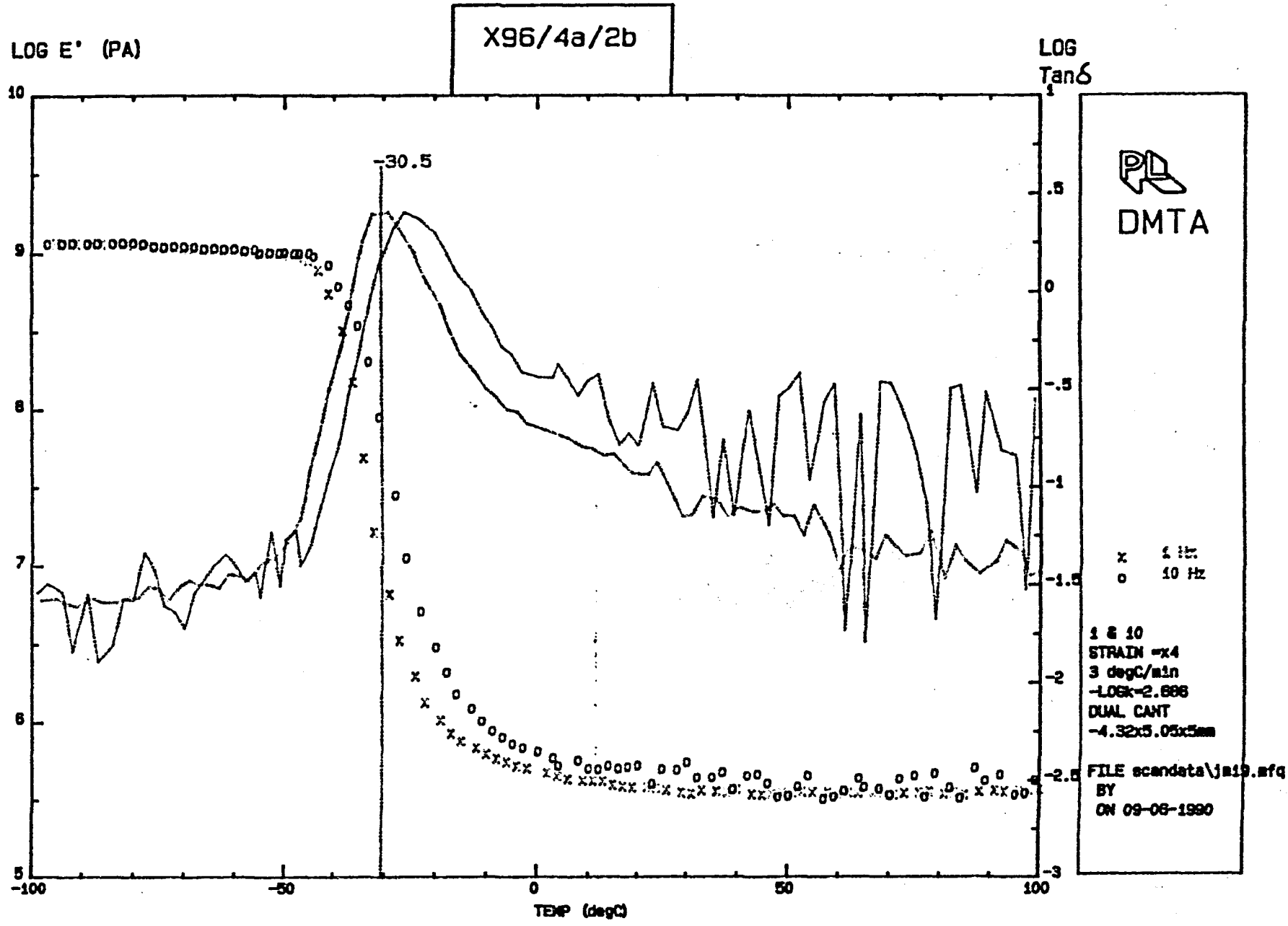

X187/1a
LOG E' (PA)
LOG Tanδ
-31
DMTA
x 1 Hz
o 10 Hz
1 & 10
STRAIN =x4
3 degC/min
-LOGk=2.655
DUAL CANT
-3.37x5.28x5mm
FILE scandata\js21.mfq
BY
ON 12-06-1990
TEMP (degC)
10
9
8
7
6
5
1
.5
0
-.5
-1
-1.5
-2
-2.5
-3
-100
-50
0
50
100

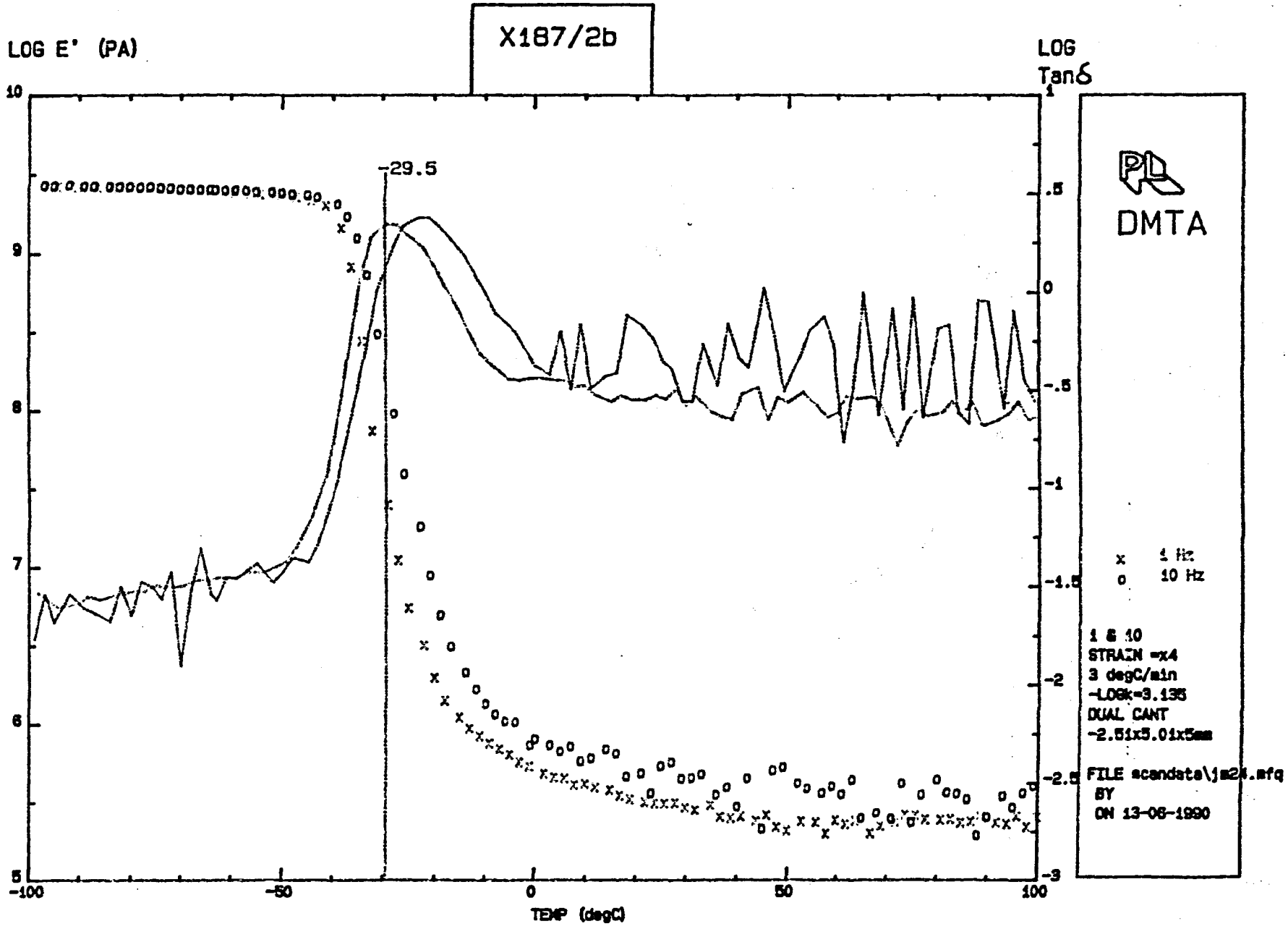

X96/2a
LOG E' (PA)
LOG Tanδ
-30
DMTA
x 1 Hz
o 10 Hz
1 & 10
STRAIN =x4
3 degC/min
-LOGk=2.785
DUAL CANT
-3.58x5.61x5mm
FILE scandata\jm17.mfq
BY
ON 08-06-1990
TEMP (degC)
10
9
8
7
6
5
1
.5
0
-.5
-1
-1.5
-2
-2.5
-3
-100
-50
0
50
100

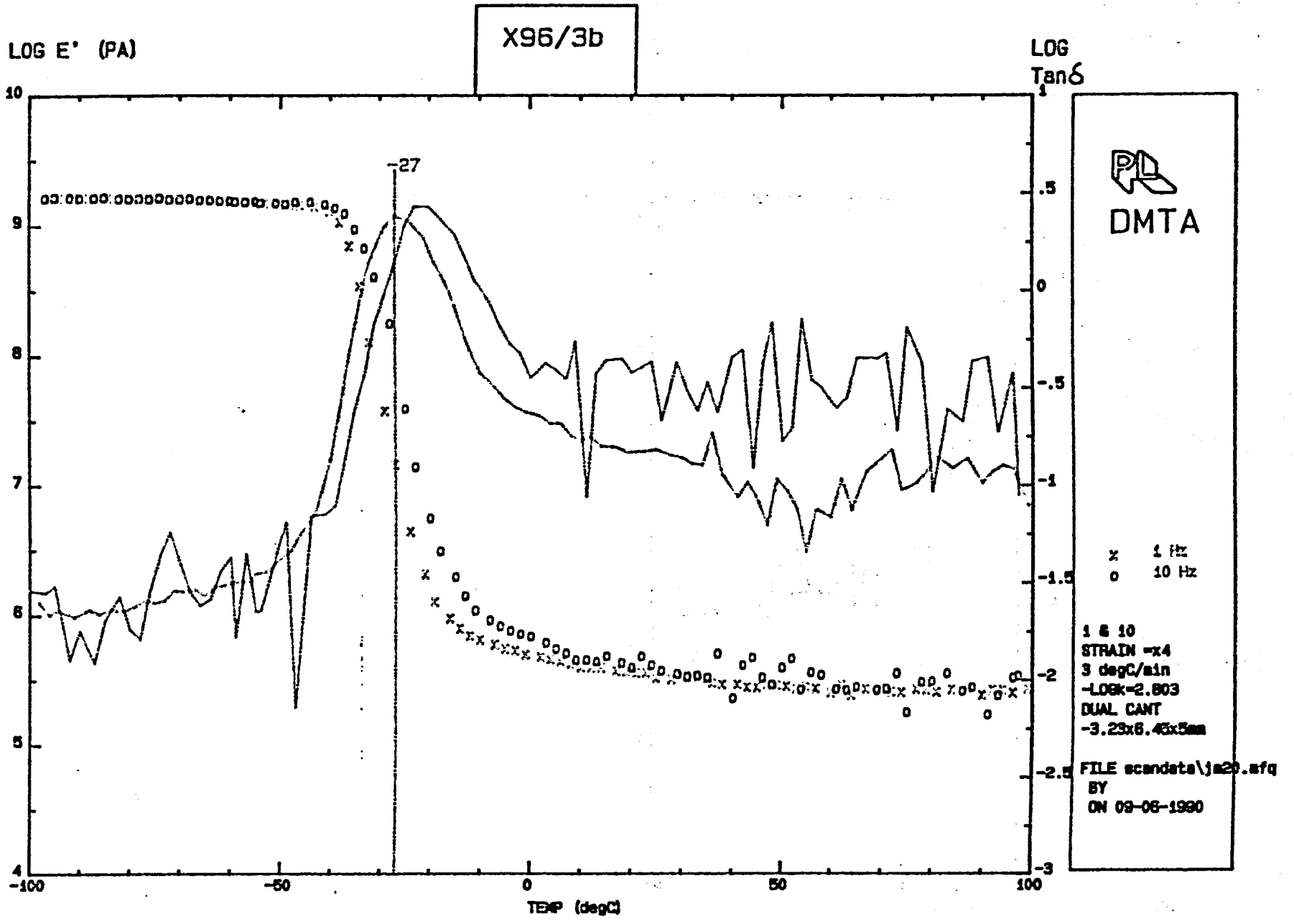

X96/3a
LOG E' (PA)
LOG Tanδ
-33
TEMP (degC)
DMTA
x 1 Hz
o 10 Hz
1 & 10
STRAIN =x4
3 degC/min
-LOGk=2.833
DUAL CANT
-3.44x5.35x5mm
FILE scandata\js27.mfa
BY
ON 04-07-1990

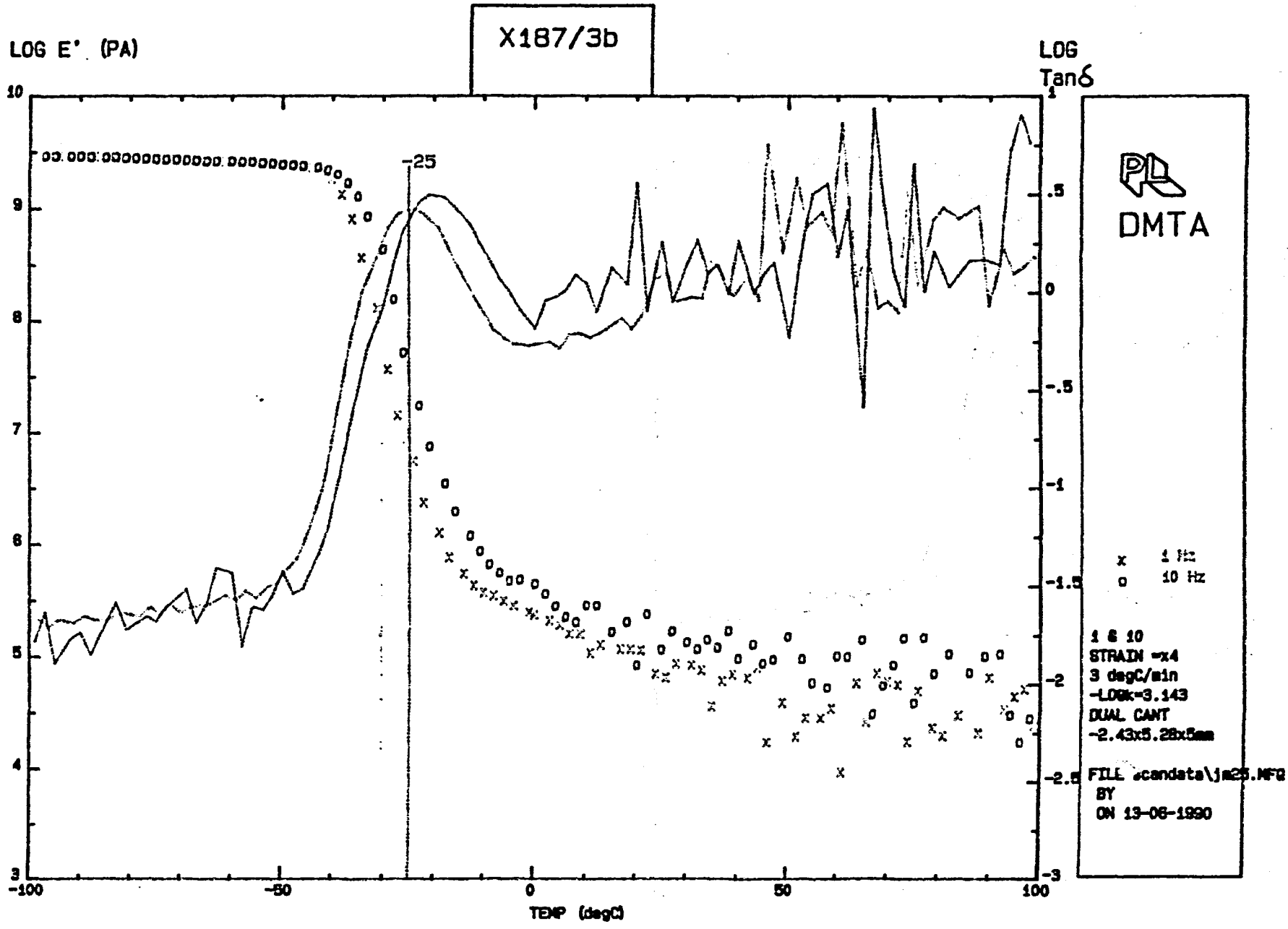

X187/2a
LOG E' (PA)
LOG Tanδ
-30
DMTA
x 1 Hz
o 10 Hz
1 & 10
STRAIN =x4
3 degC/min
-LOGk=2.918
DUAL CANT
-3.06x5.43x5mm
FILE scandata\js22.mfq
ON 12-06-1990
TEMP (degC)
10
9
8
7
6
5
1
.5
0
-.5
-1
-1.5
-2
-2.5
-3
-100
-50
0
50
100

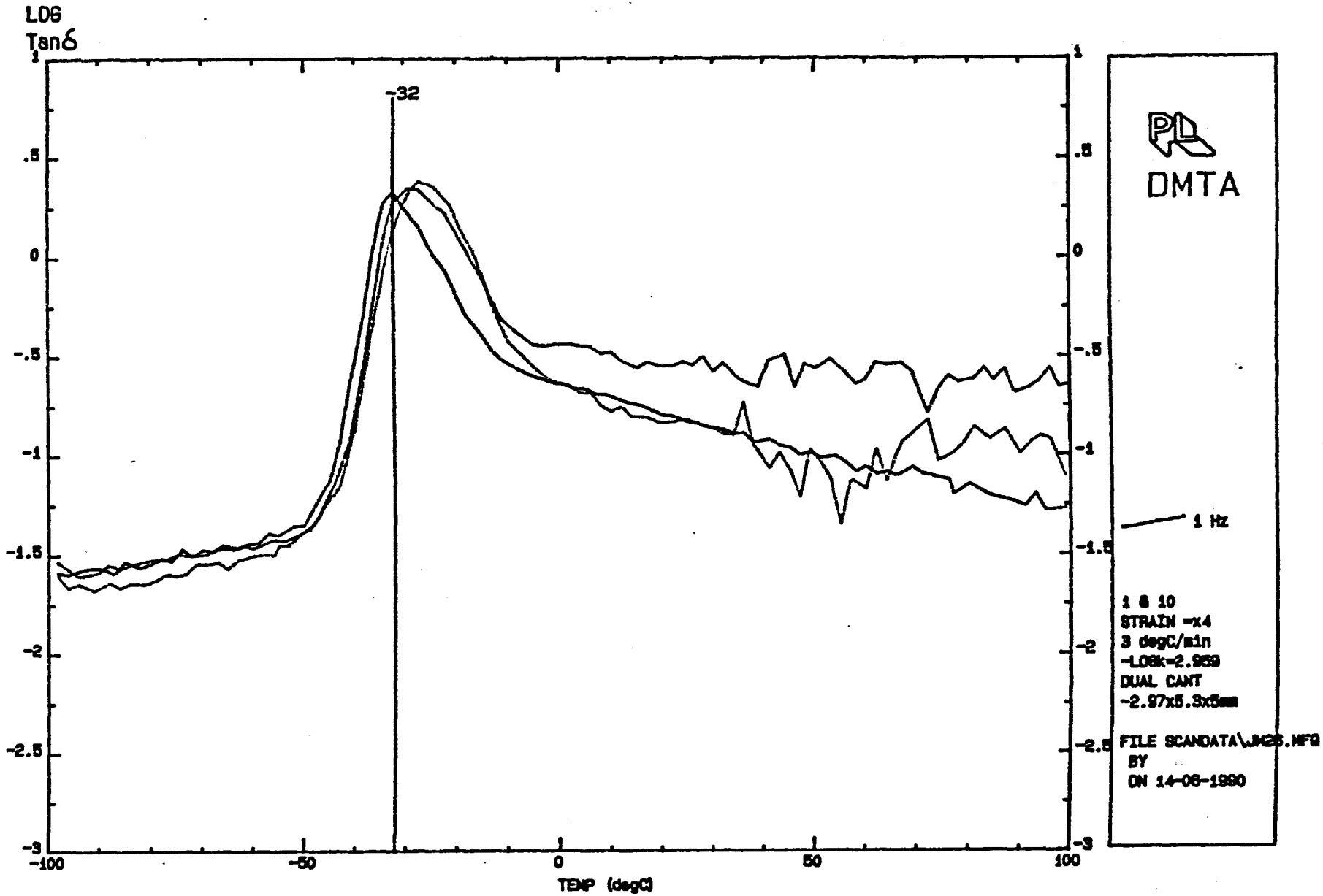

X187/3a
LOG E' (PA)
LOG Tanδ
10
9
8
7
6
5
1
.5
0
-.5
-1
-1.5
-2
-2.5
-3
-30
-100
-50
0
50
100
TEMP (degC)
DMTA
x 1 Hz
o 10 Hz
1 & 10
STRAIN =x4
3 degC/min
-LOGk=3.065
DUAL CANT
-2.77x4.79x5mm
FILE scandata\jm23.mfq
BY
ON 12-06-1990

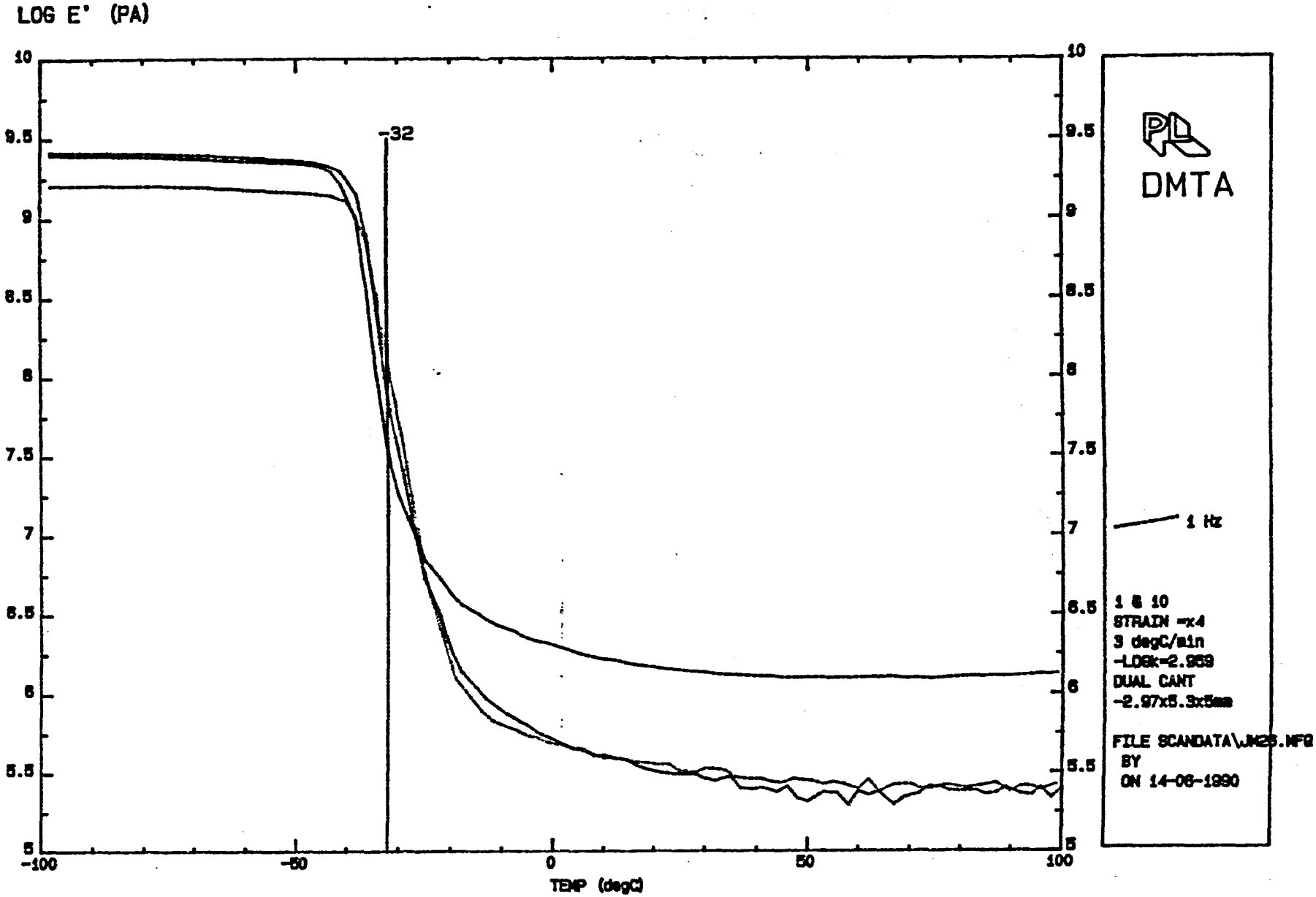

X96/4a/2b
LOG E' (PA)
LOG Tan δ
-30.5
DMTA
x 1 Hz
o 10 Hz
1 & 10
STRAIN =x4
3 degC/min
-LOGk=2.686
DUAL CANT
-4.32x5.05x5mm
FILE scandata\ja19.mfq
BY
ON 09-06-1990
TEMP (degC)


X187/2b
LOG E' (PA)
LOG Tanδ
-29.5
DMTA
x 1 Hz
o 10 Hz
1 & 10
STRAIN =x4
3 degC/min
-LOGk=3.135
DUAL CANT
-2.51x5.01x5mm
FILE scandata\js24.mfq
BY
ON 13-06-1990
TEMP (degC)
10
9
8
7
6
5
1
.5
0
-.5
-1
-1.5
-2
-2.5
-3
-100
-50
0
50
100


X96/3b
LOG E' (PA)
LOG Tanδ
-27
DMTA
x 1 Hz
o 10 Hz
1 & 10
STRAIN =x4
3 degC/min
-LOGk=2.803
DUAL CANT
-3.23x6.46x5mm
FILE scandata\js20.sfq
BY
ON 09-06-1990
TEMP (degC)
10
9
8
7
6
5
4
1
.5
0
-.5
-1
-1.5
-2
-2.5
-3
-100
-50
0
50
100


X187/3b
LOG E' (PA)
LOG Tanδ
DMTA
-25
TEMP (degC)
1 Hz
10 Hz
1 6 10
STRAIN =x4
3 degC/min
-LOGk=3.143
DUAL CANT
-2.43x5.28x5mm
BY
ON 13-06-1990


LOG
Tanδ
-32
DMTA
1 Hz
1 & 10
STRAIN =x4
3 degC/min
-LOGk=2.959
DUAL CANT
-2.97x5.3x5mm
FILE SCANDATA\JM25.MFD
BY
ON 14-06-1990
TEMP (degC)
No Plasticizer
70% of Plasticizer
100phr of Plasticiser



No Plasticizer

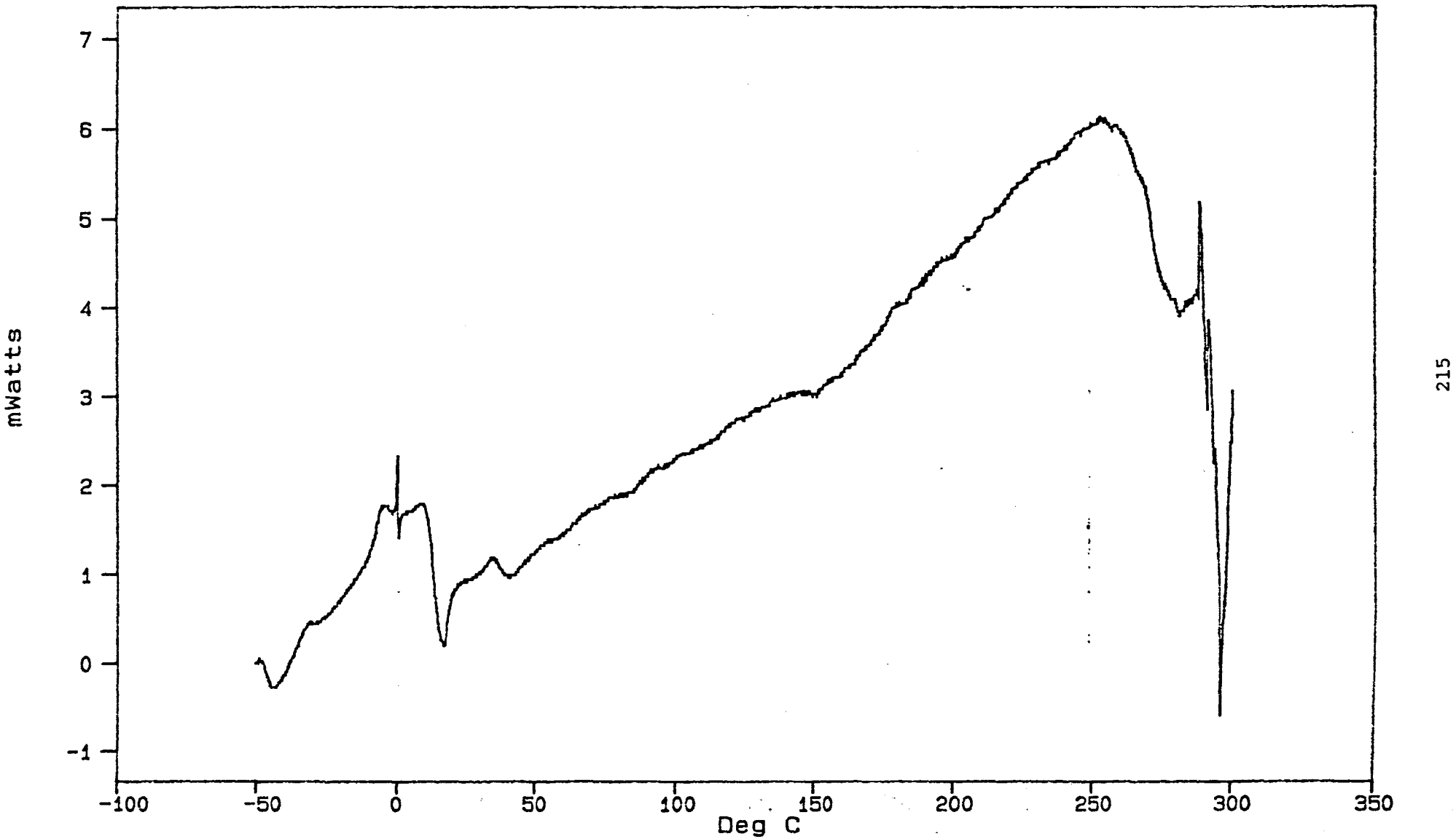
70% of Plasticizer

100% phr of Plasticiser

DSC 700
STANTON REDCROFT

SMPL ID : CONTROL
RUN ID :
SIZE : 10.500 mg
OPERATOR:

DATE RUN: Jun/12/1990
GASES :
SOURCE : LAB
COMMENT :

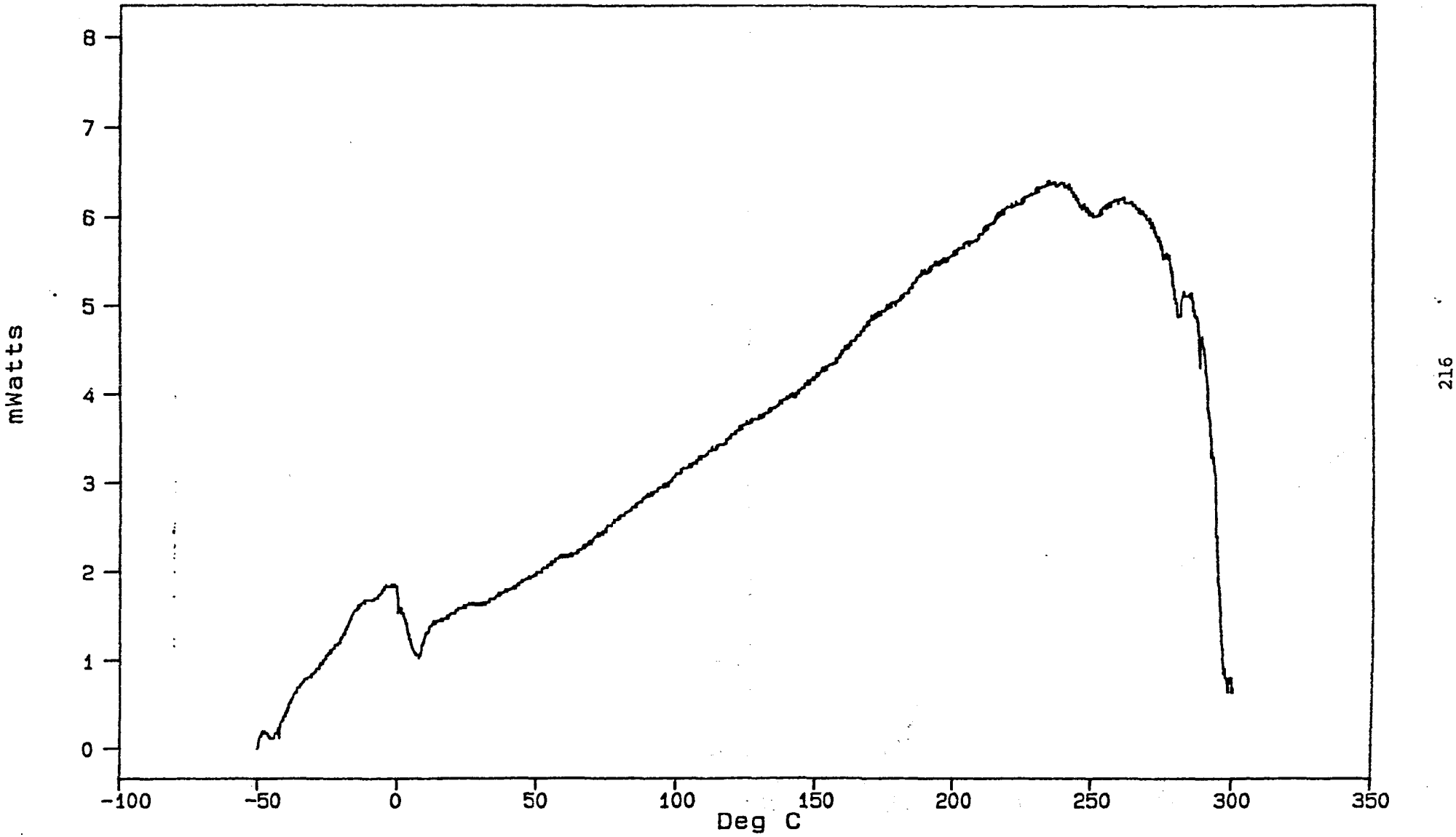


VERSION: C4.20

DSC 700
STANTON REDCROFT

SMPL ID : X187/1a
RUN ID :
SIZE : 7.900 mg
OPERATOR:

DATE RUN: Jun/11/1990
GASES :
SOURCE : LAB
COMMENT :



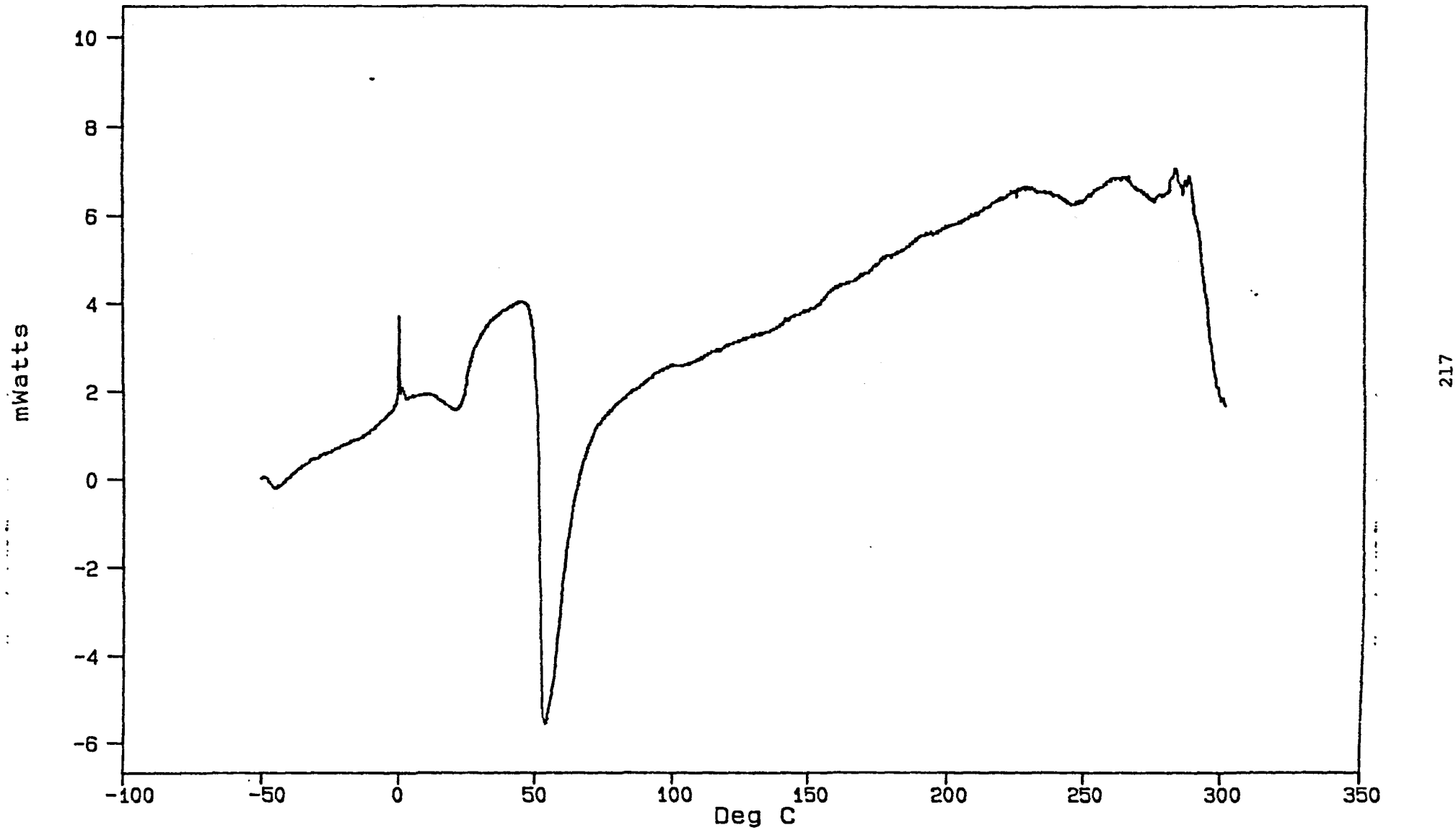
216

VERSION: C4.20

DSC 700
STANTON REDCROFT

SMPL ID : X96/2a
RUN ID :
SIZE : 10.100 mg
OPERATOR:

DATE RUN: Jun/07/1990
GASES :
SOURCE : LAB
COMMENT :



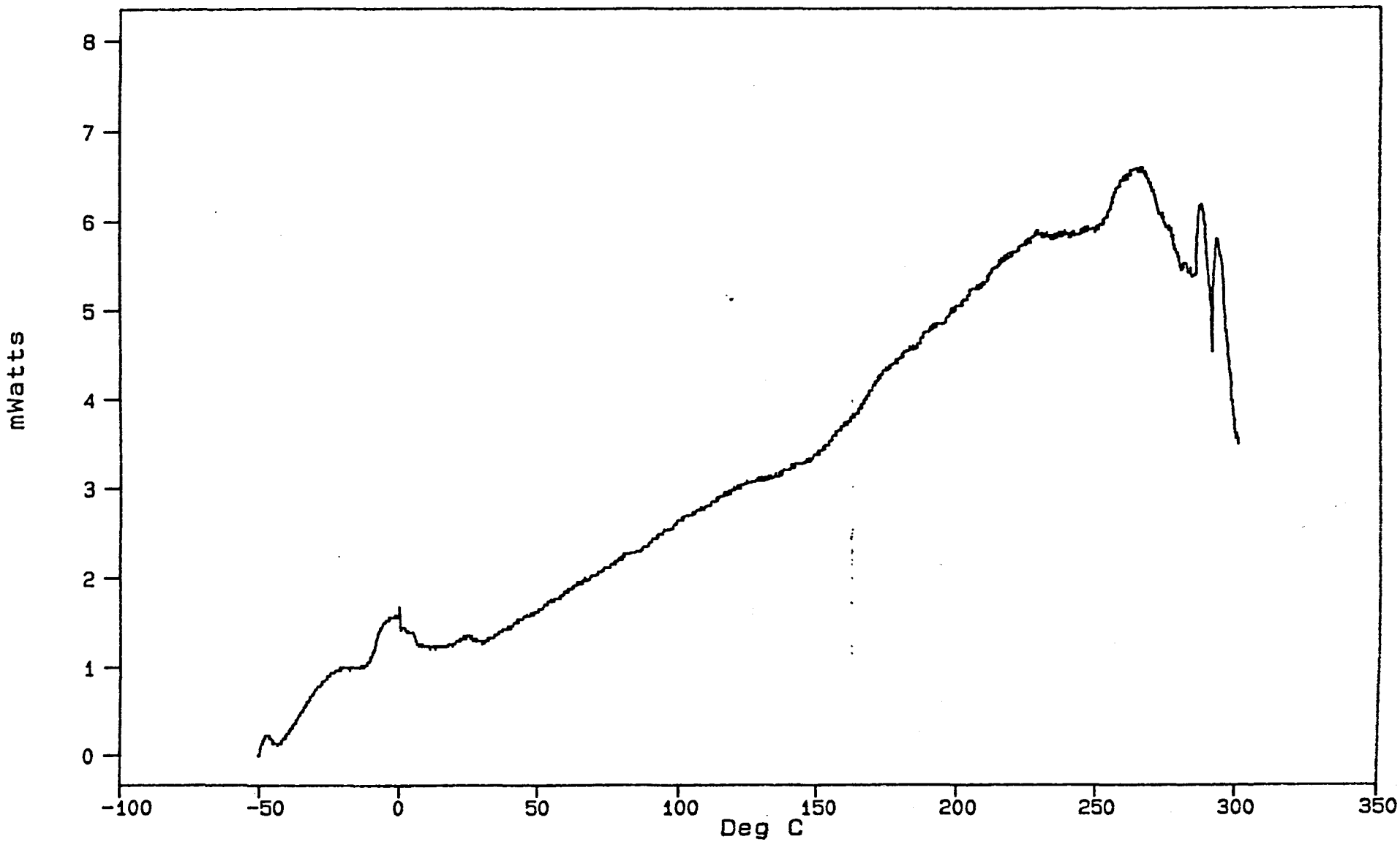
217

VERSION: C4.20

DSC 700
STANTON REDCROFT

SMPL ID : X187/2a
RUN ID :
SIZE : 10.200 mg
OPERATOR:

DATE RUN: Jun/11/1990
GASES :
SOURCE : LAB
COMMENT :



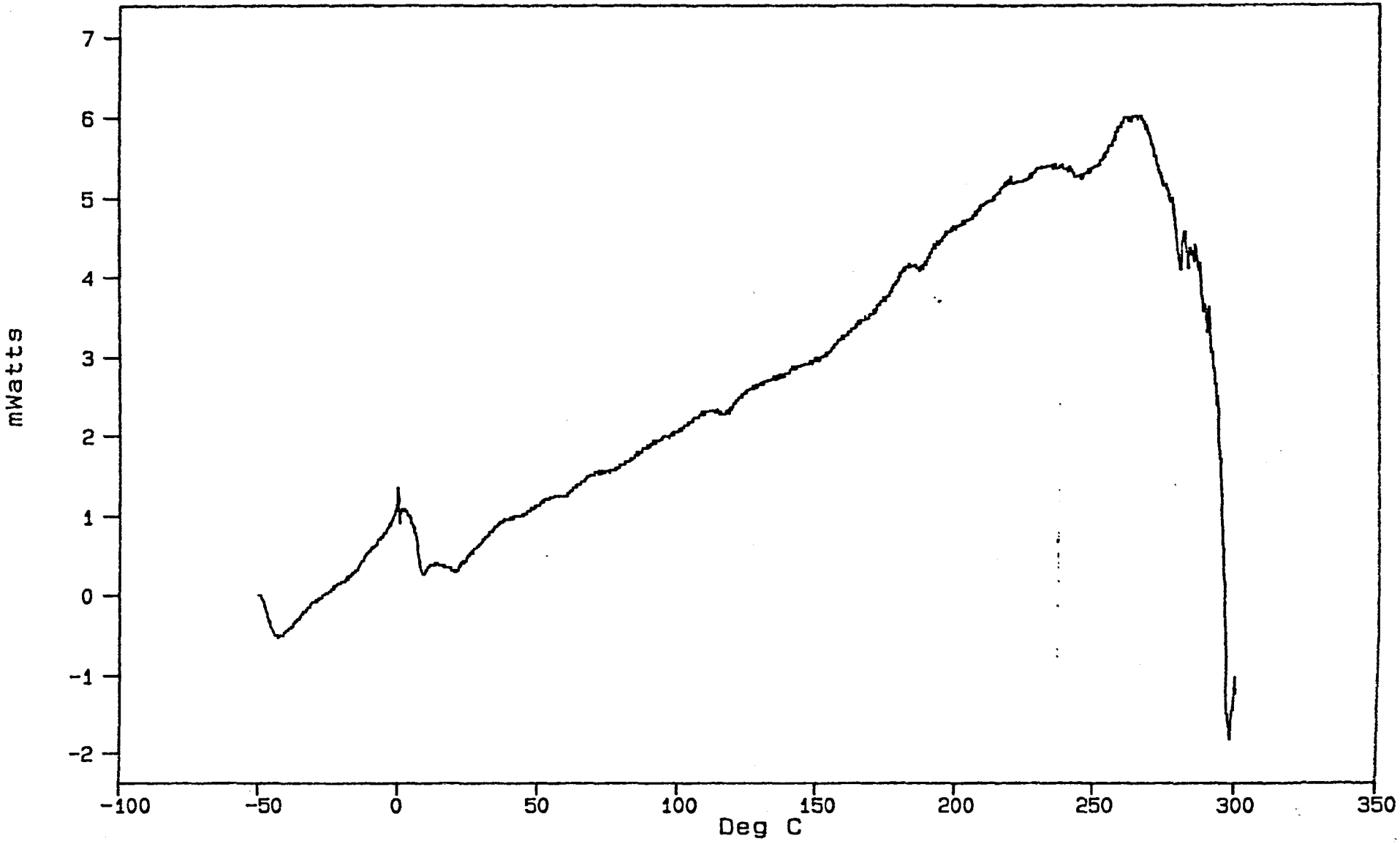
218

VERSION: C4.20

DSC 700
STANTON REDCROFT

SMPL ID : X96/3a
RUN ID :
SIZE : 11.800 mg
OPERATOR:

DATE RUN: Jun/08/1990
GASES :
SOURCE : LAB
COMMENT :



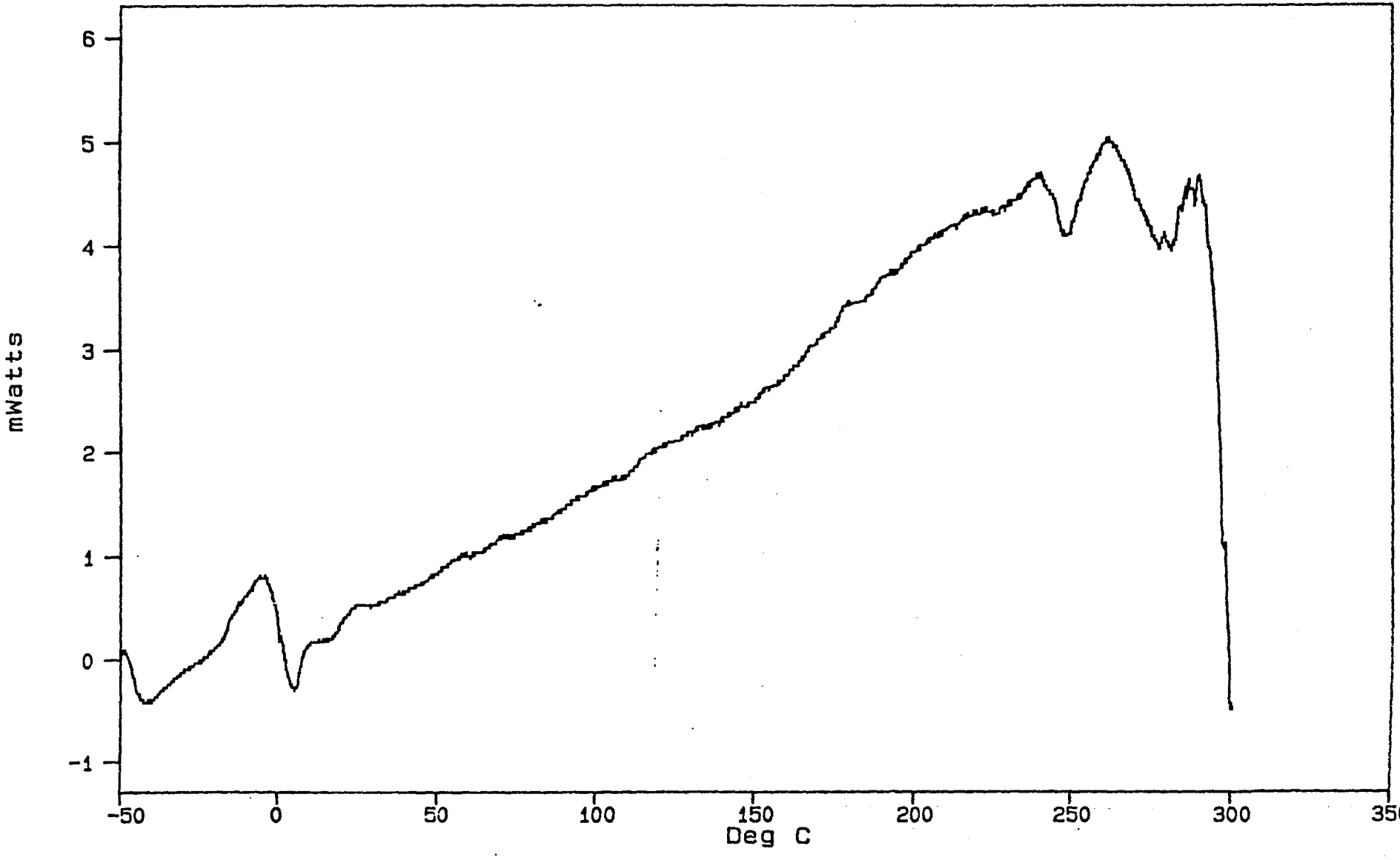
VERSION: C4.20

DSC 700

STANTON REDCROFT

SMPL ID : X187/3a
RUN ID :
SIZE : 11.100 mg
OPERATOR:

DATE RUN: Jun/11/1990
GASES :
SOURCE : LAB
COMMENT :



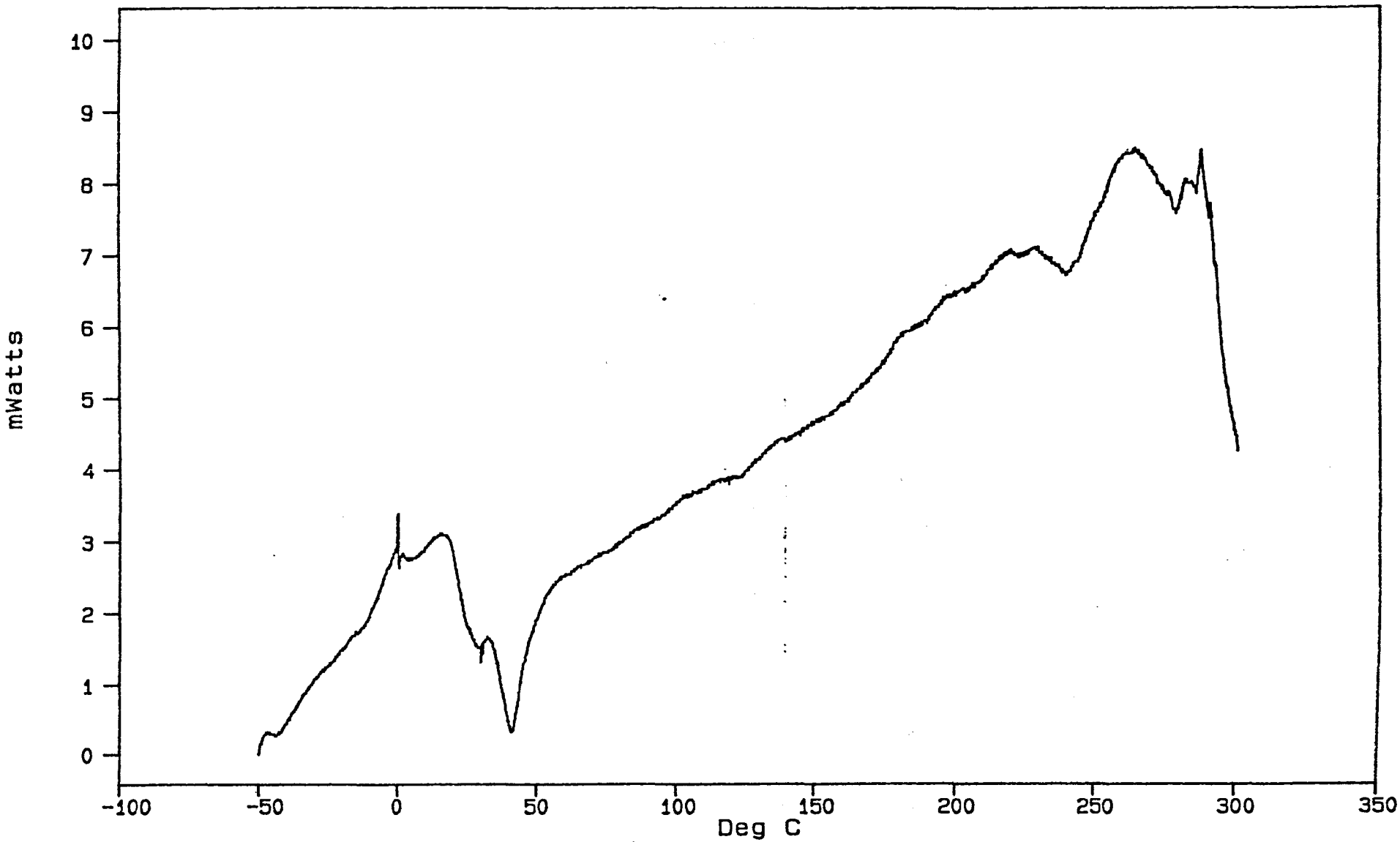
VERSION: C4.20

DSC 700

STANTON REDCROFT

SMPL ID : X96/4a/2b
RUN ID :
SIZE : 11.200 mg
OPERATOR:

DATE RUN: Jun/08/1990
GASES :
SOURCE : LAB
COMMENT :



221

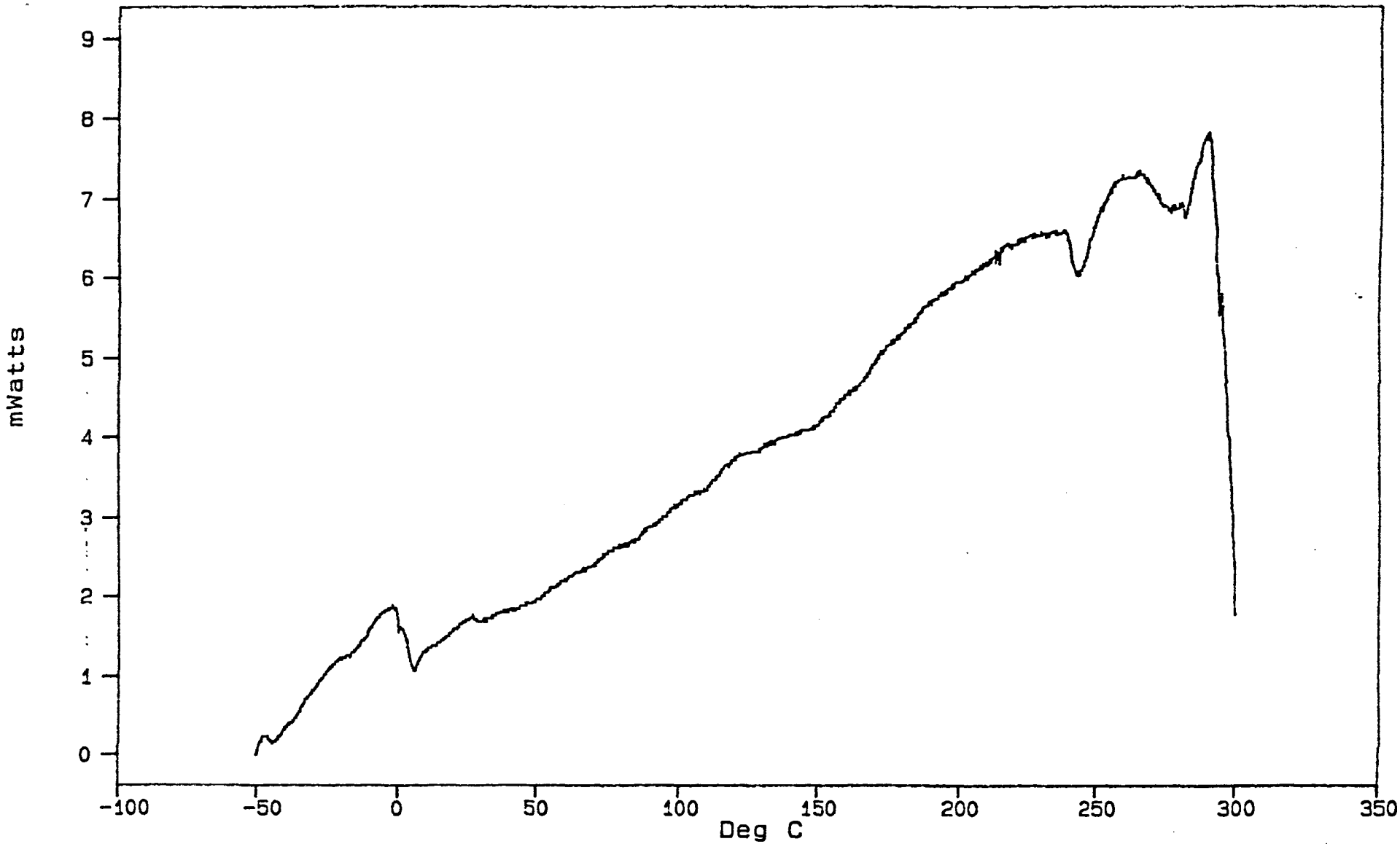
VERSION: C4.20

DSC 700

STANTON REDCROFT

SMPL ID : X187/2b
RUN ID :
SIZE : 12.700 mg
OPERATOR:

DATE RUN: Jun/12/1990
GASES :
SOURCE : LAB
COMMENT :



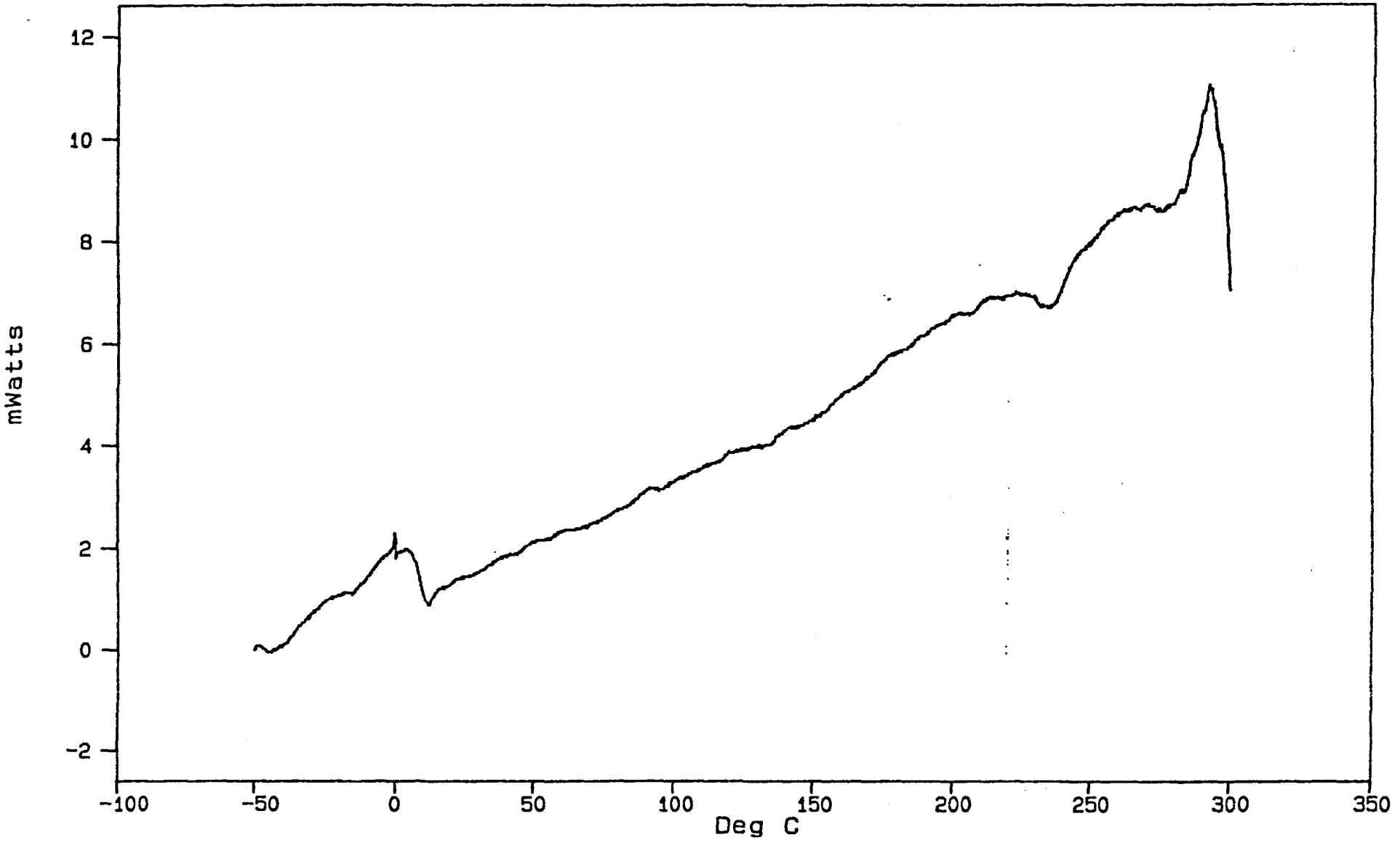
222

VERSION: C4.20

DSC 700
STANTON REDCROFT

SMPL ID : X96/3b
RUN ID :
SIZE : 12.000 mg
OPERATOR:

DATE RUN: Jun/08/1990
GASES :
SOURCE : LAB
COMMENT :



223

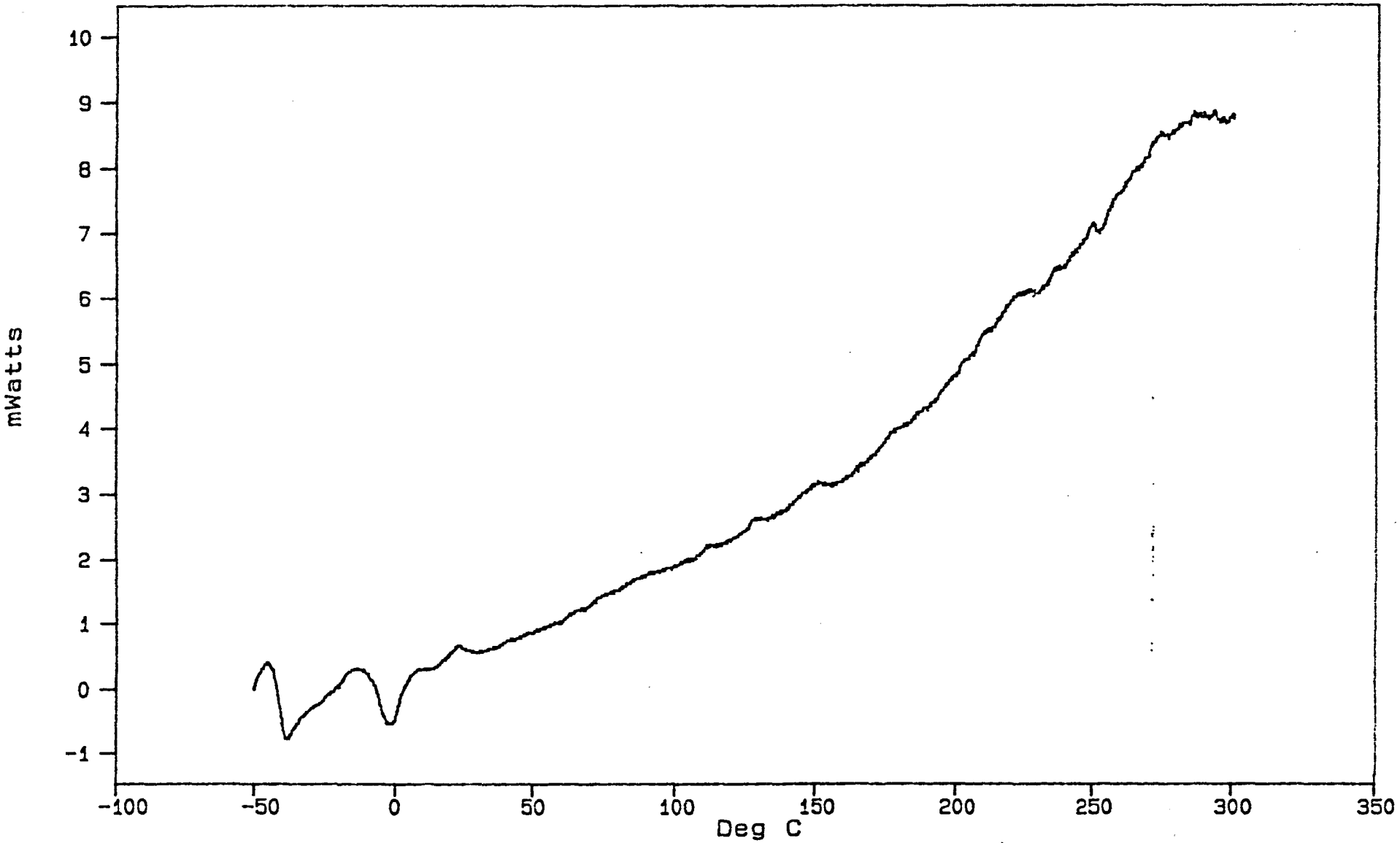
VERSION: C4.20

DSC 700

STANTON REDCROFT

SMPL ID : SANTICIZER 278
RUN ID :
SIZE : 14.700 mg
OPERATOR:

DATE RUN: Jun/13/1990
GASES :
SOURCE : LAB SAMPLE
COMMENT :



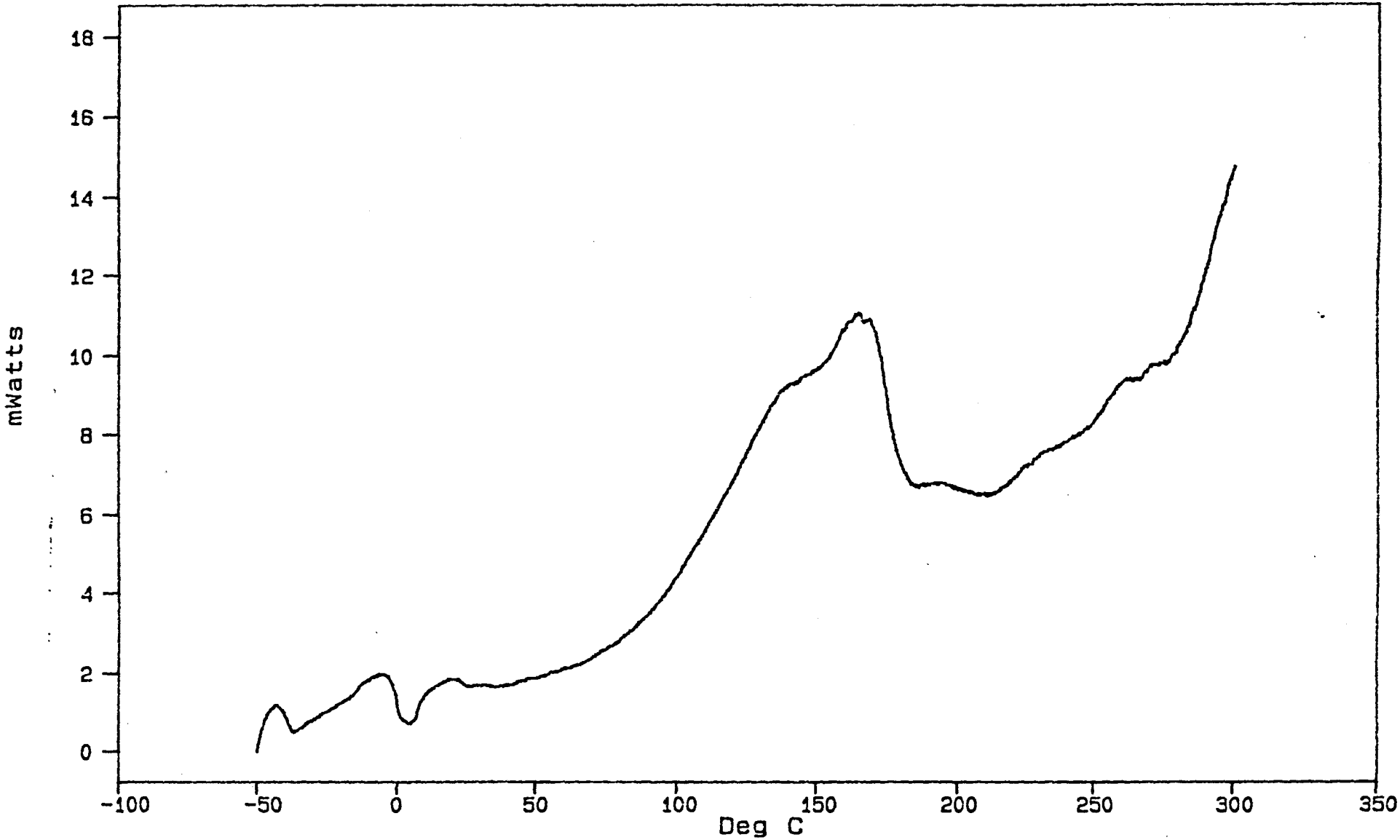
224

VERSION: C4.20

DSC 700
STANTON REDCROFT

SMPL ID : MnO2 PASTE
RUN ID :
SIZE : 22.200 mg
OPERATOR:

DATE RUN: Jun/13/1990
GASES :
SOURCE :
COMMENT : X96 cure paste

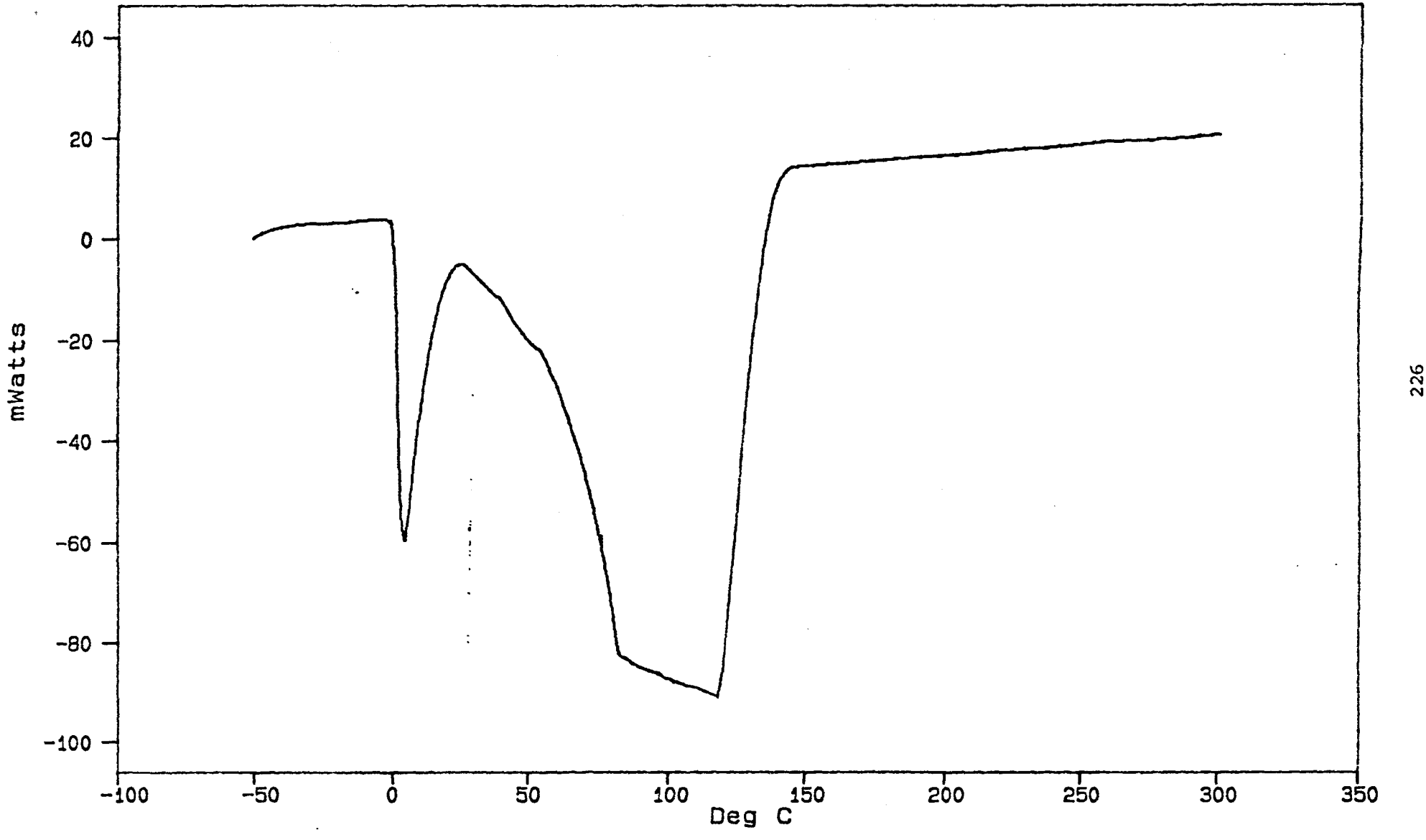


VERSION: C4.20

DSC 700
STANTON REDCROFT

SMPL ID : WATER
RUN ID :
SIZE : 16.100 mg
OPERATOR:

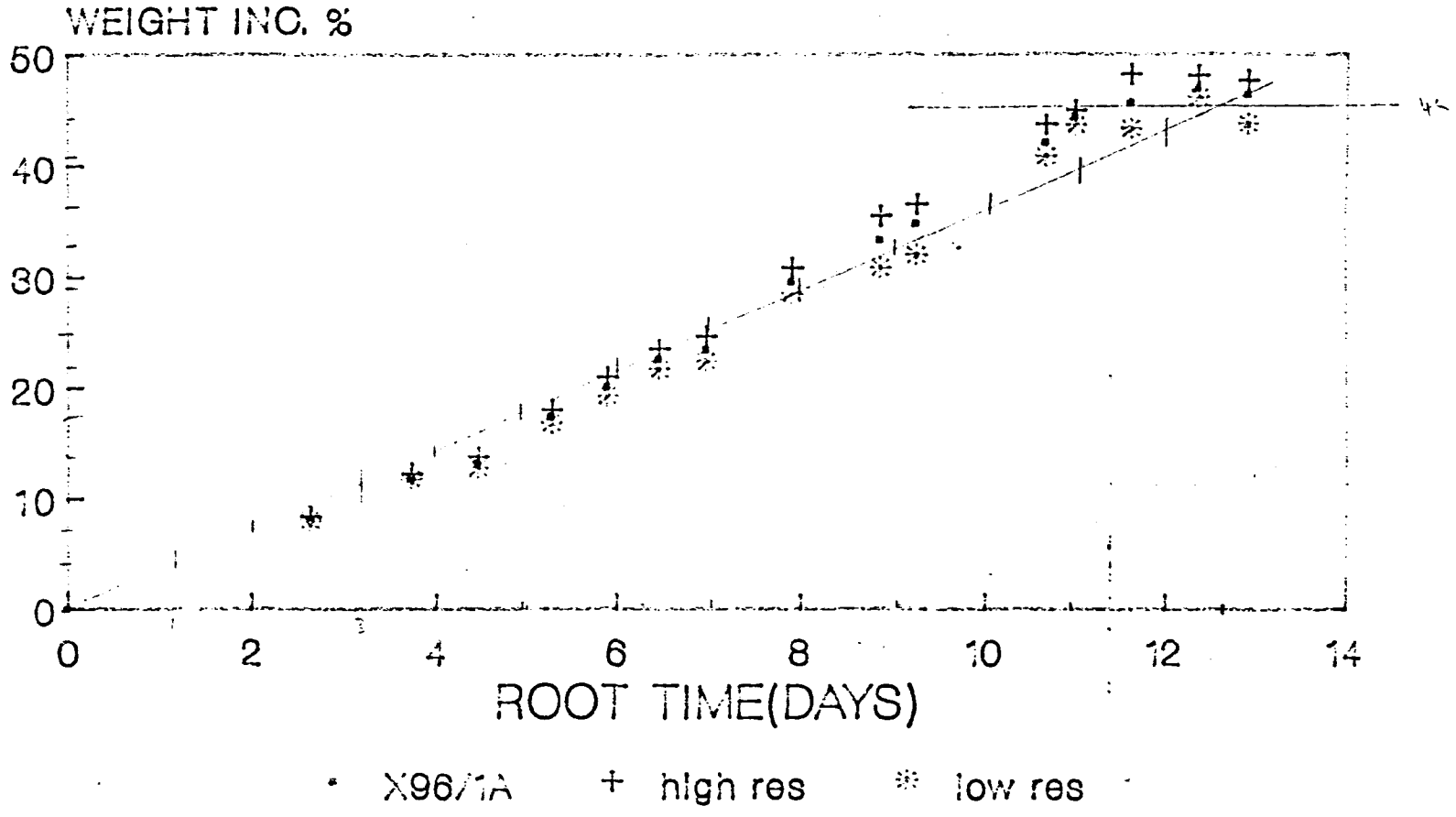
DATE RUN: Jun/13/1990
GASES :
SOURCE : LAB
COMMENT :



226

VERSION: C4.20

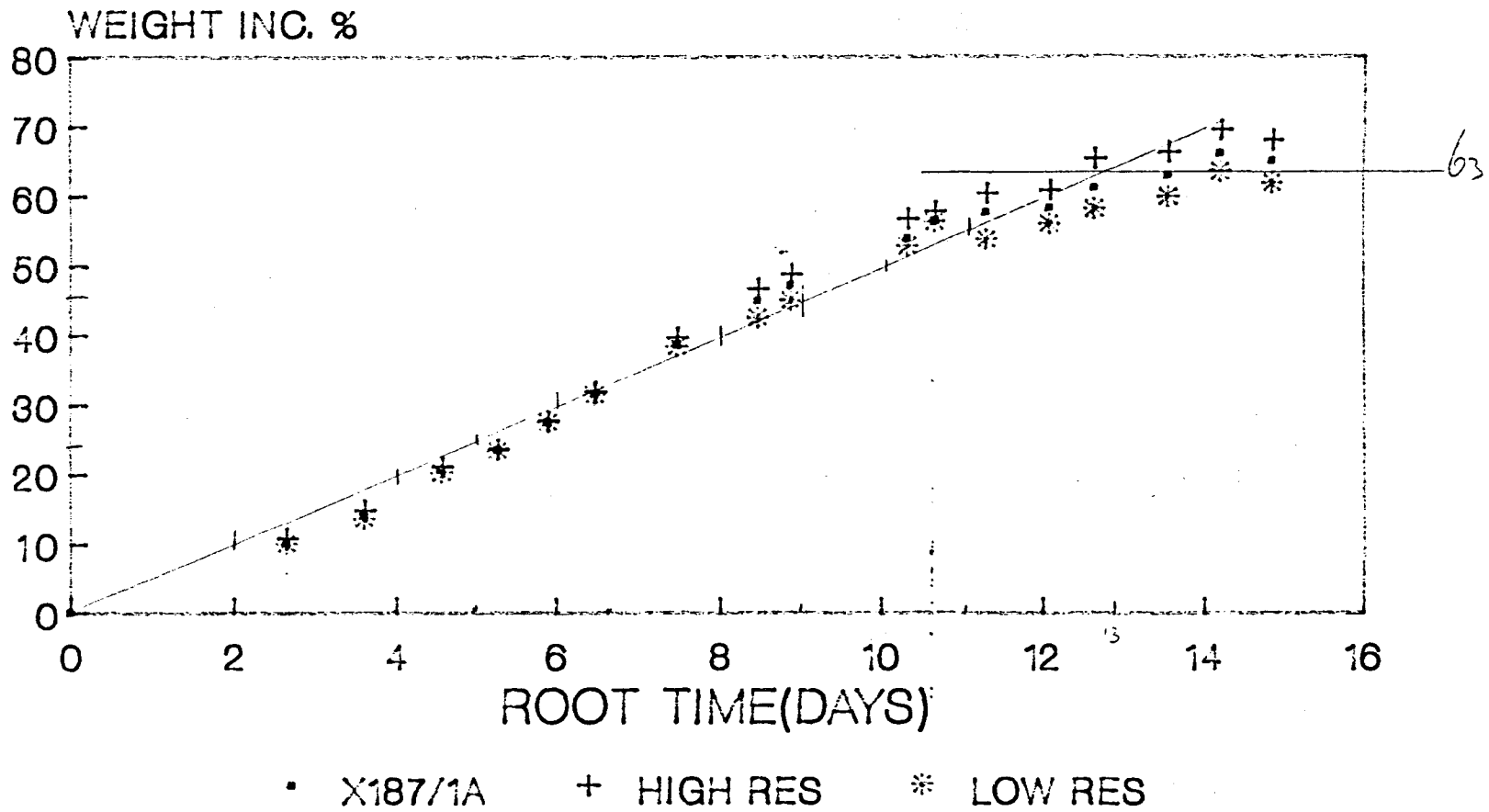
water absorption
weight increase % v root time



227

X96/1A X1

water absorption
weight increase % v root time

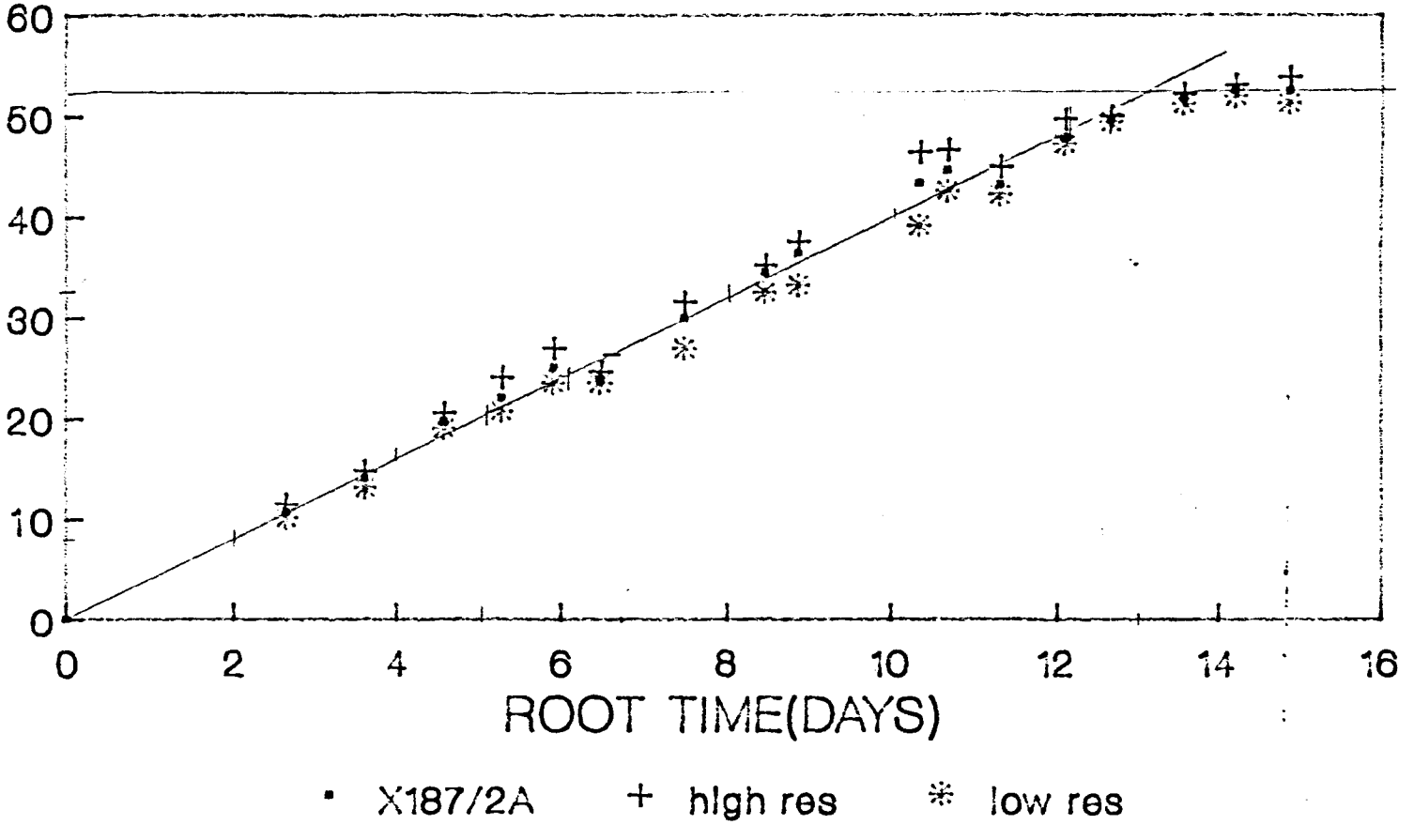


228

X187/1A X2

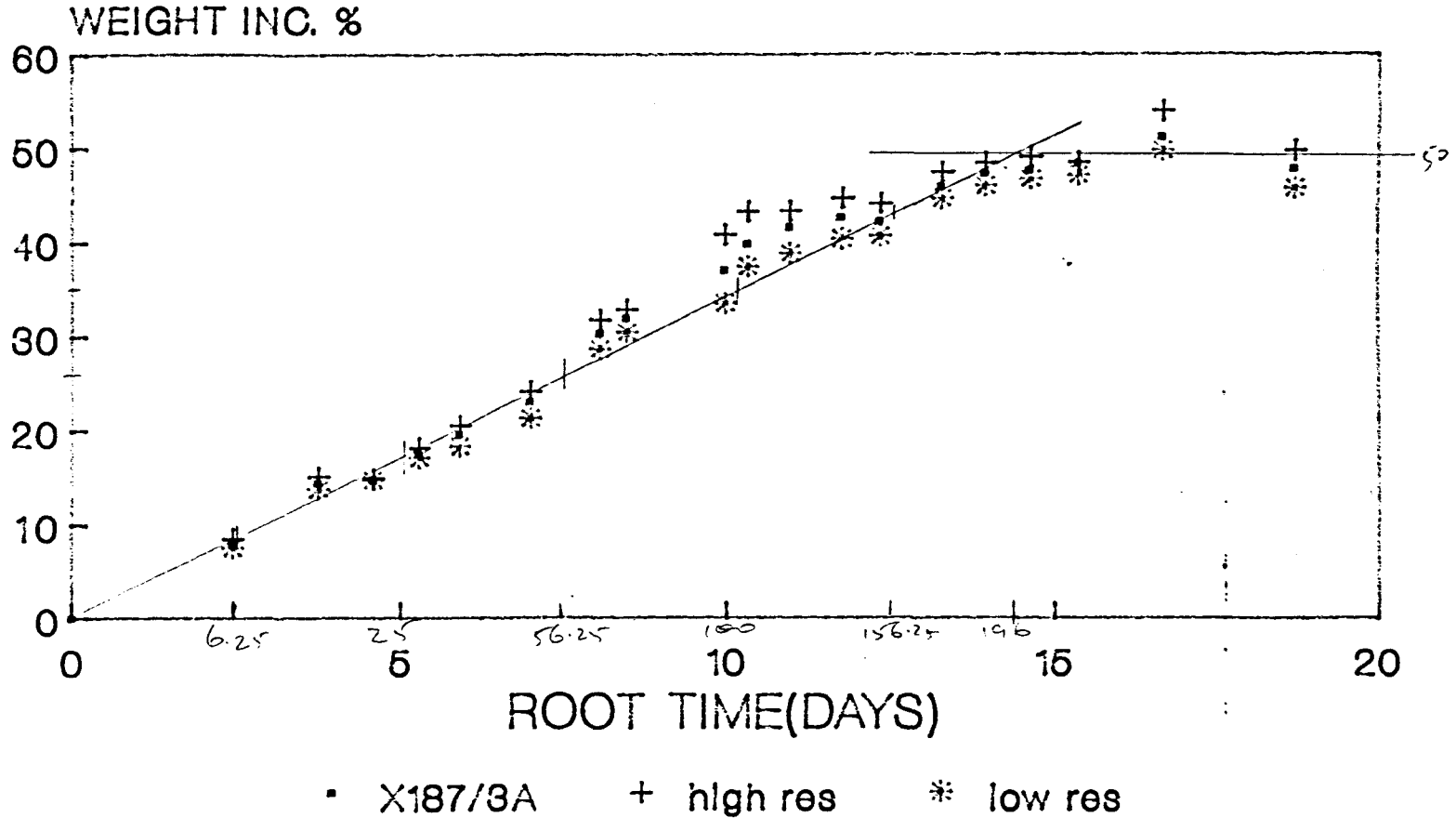
water absorption

weight increase % v root time



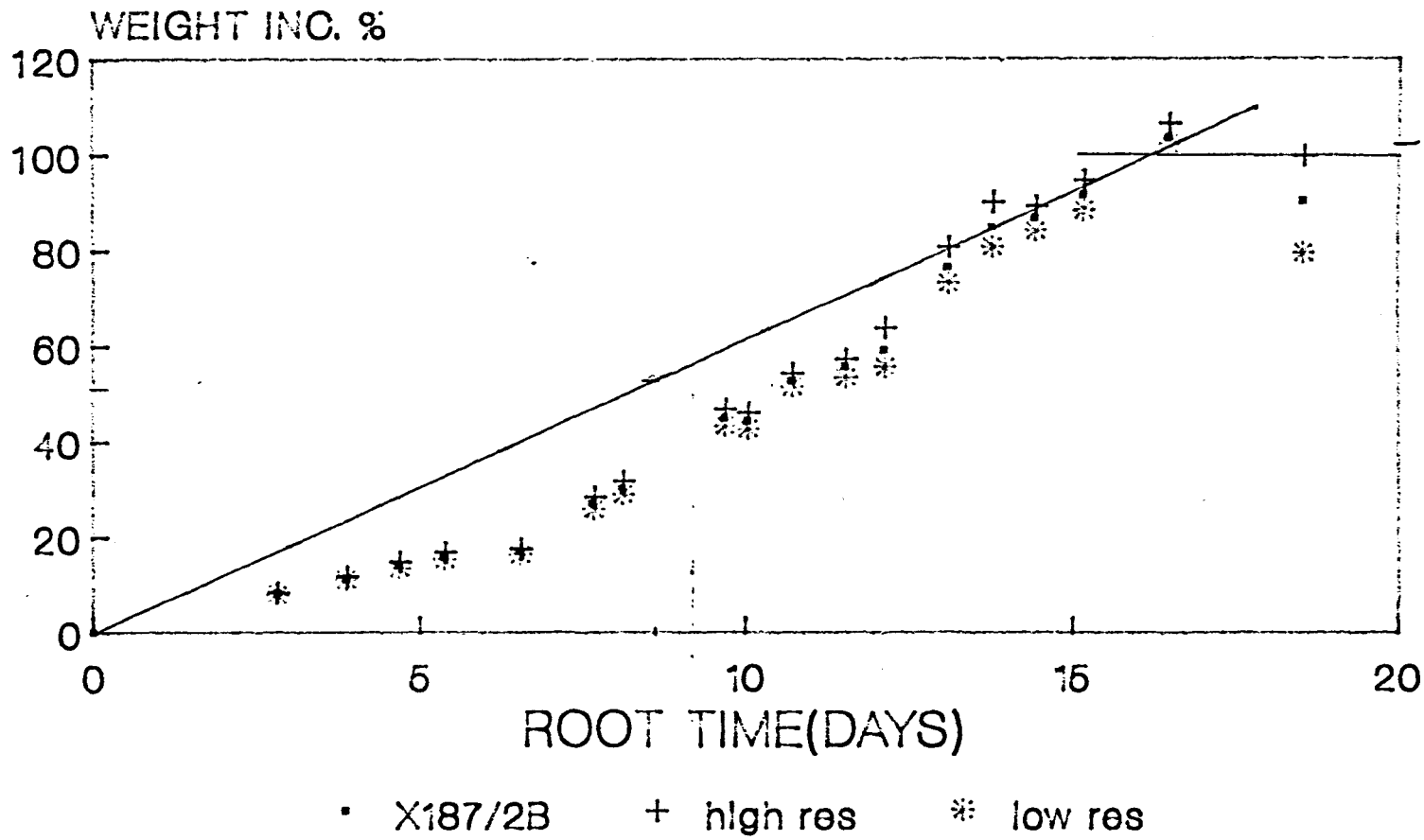
X187/2A X3

water absorption
weight increase % v root time



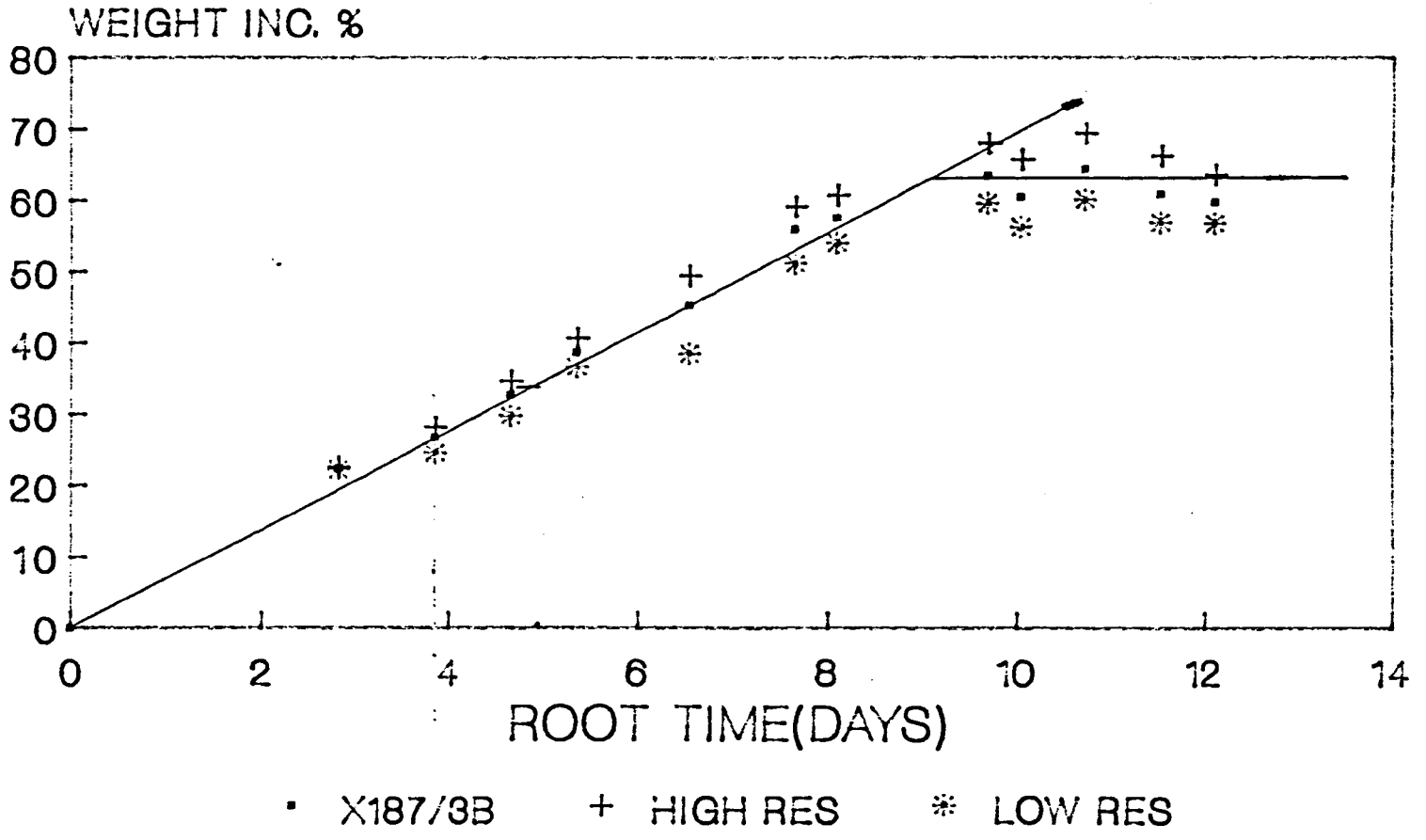
X187/3A X4

water absorption
weight increase % v root time



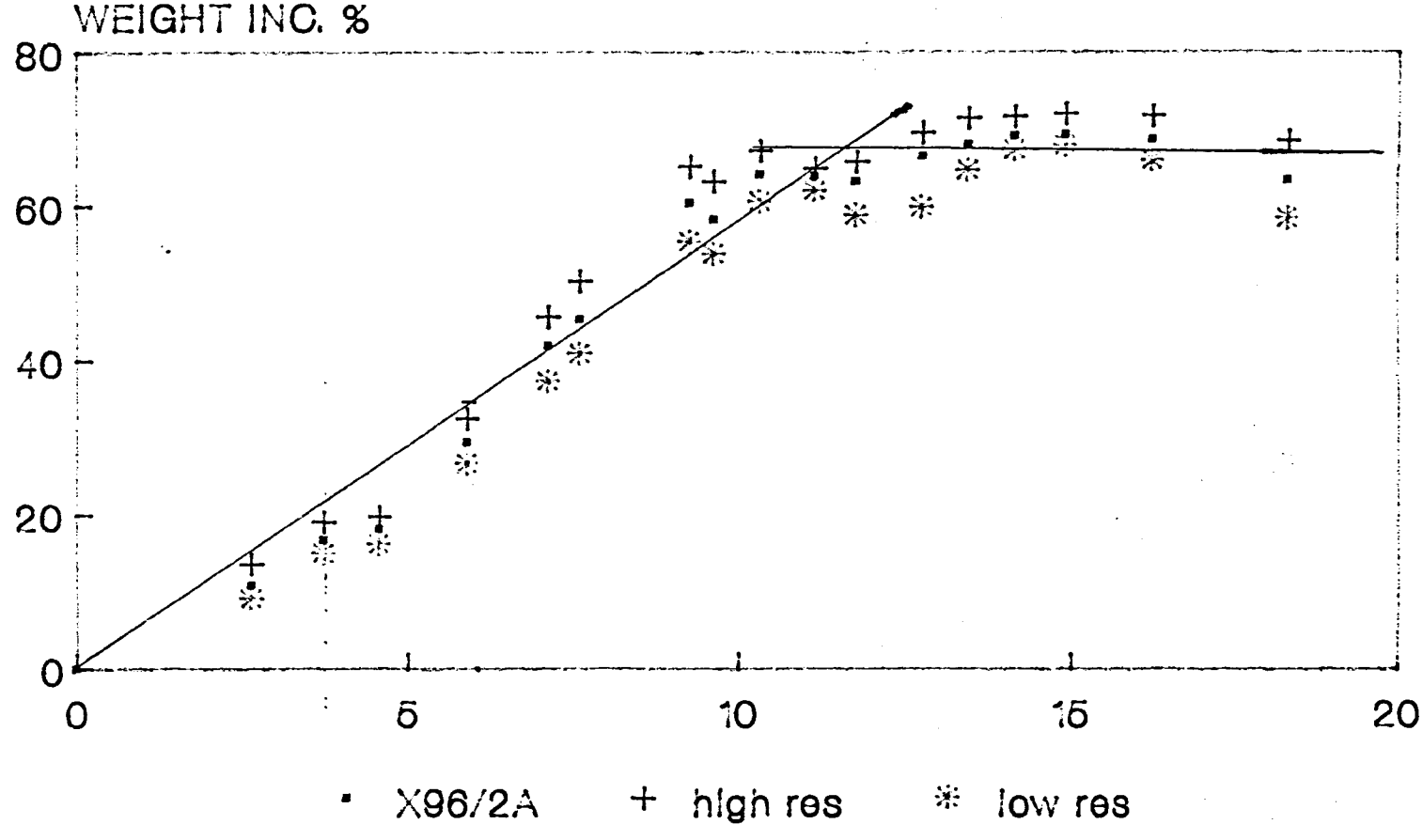
X187/2B X5

water absorption
weight increase % v root time



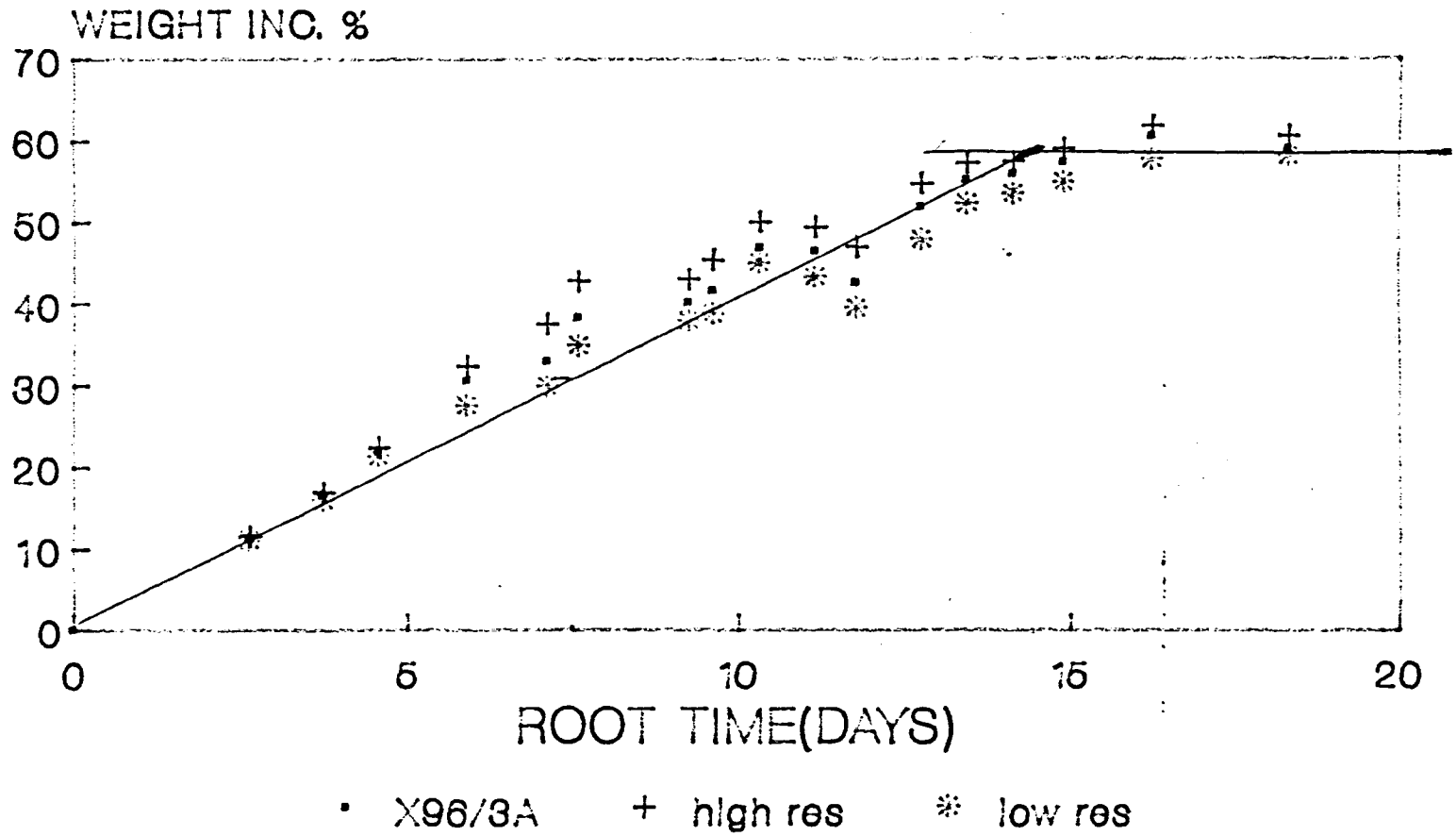
X187/3B X6

water absorption
weight increase % v root time



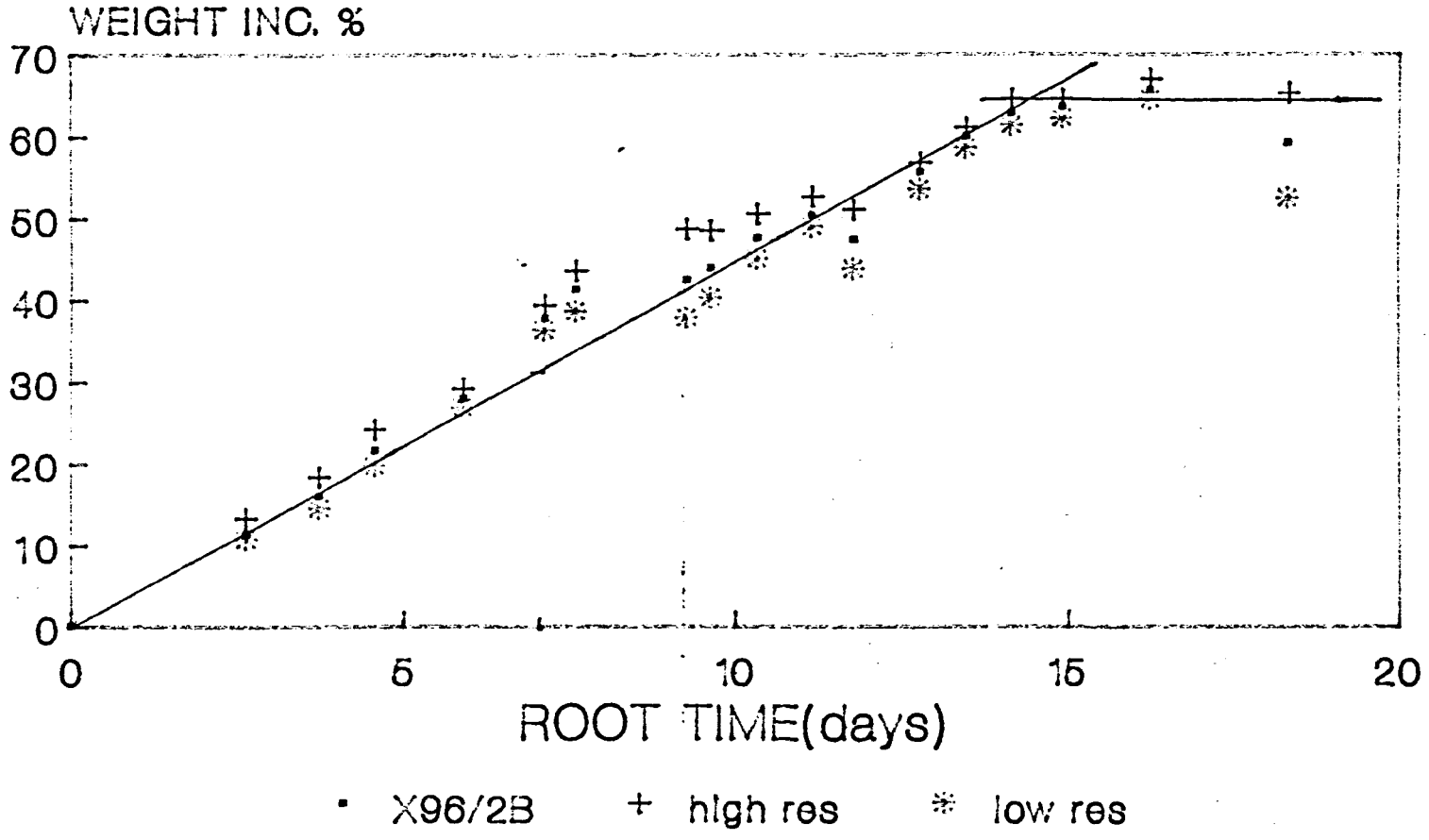
X96/2A X7

water absorption
weight increase % v root time

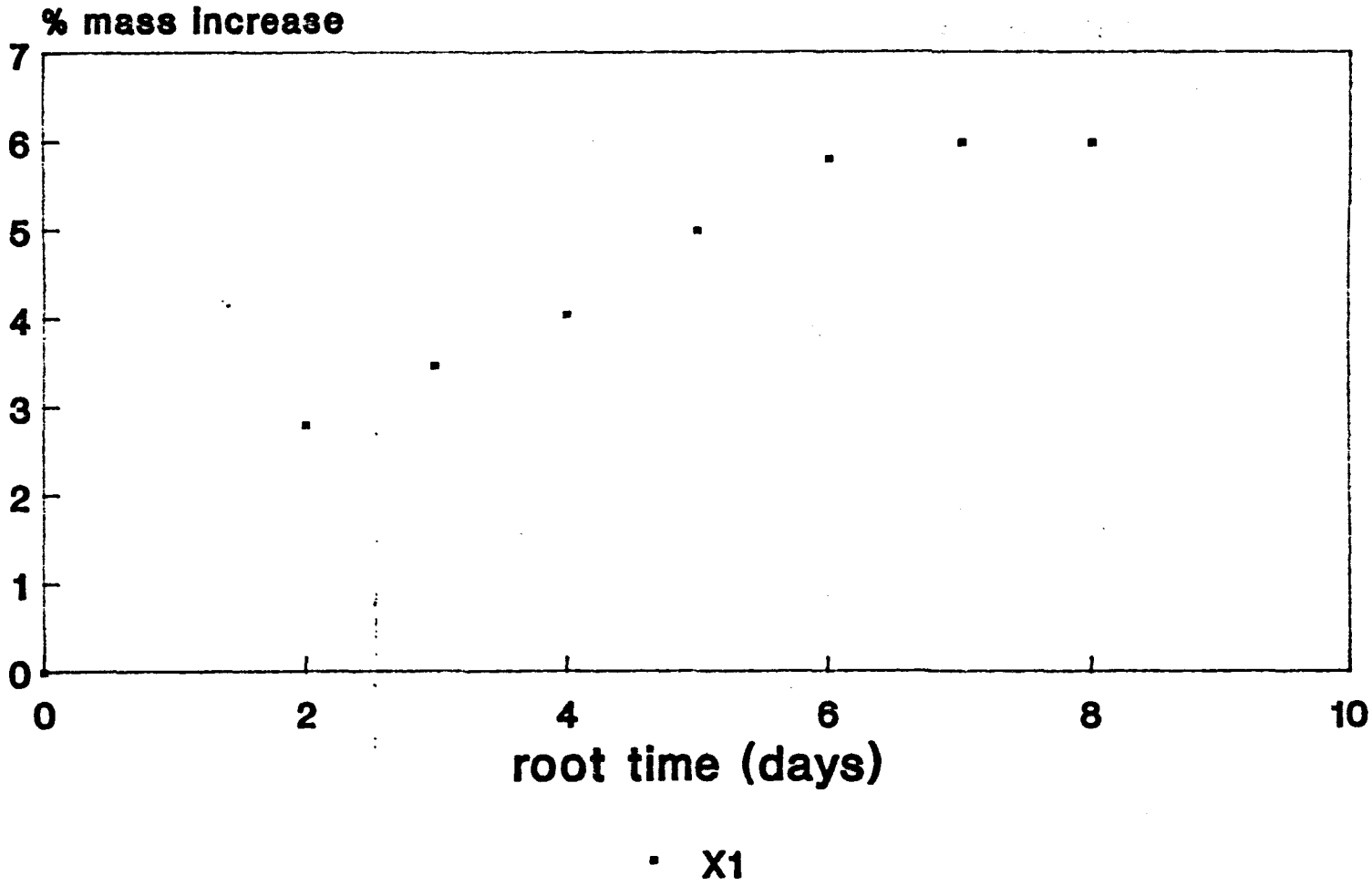


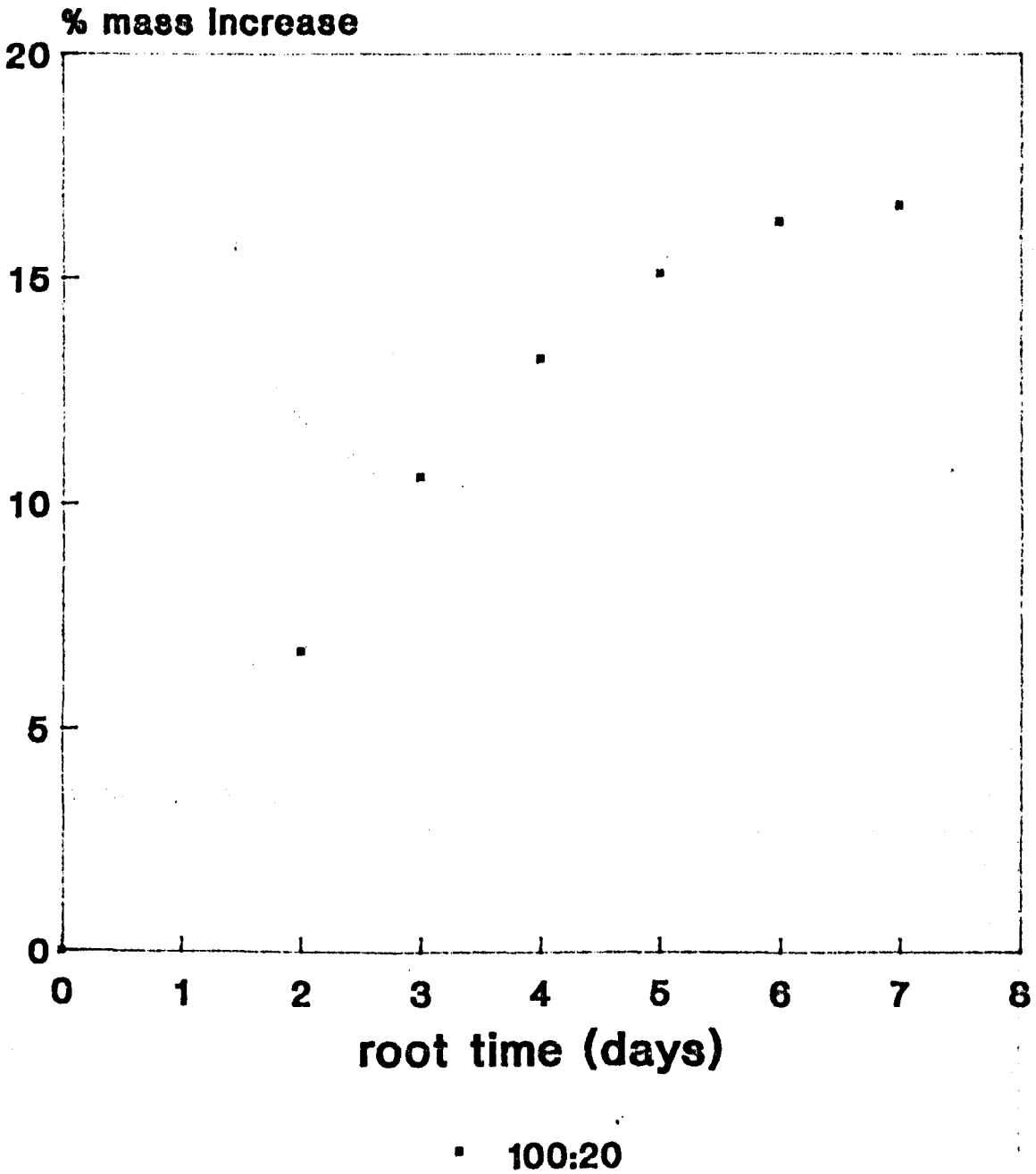
X96/3A X8

water absorption
weight increase % v root time

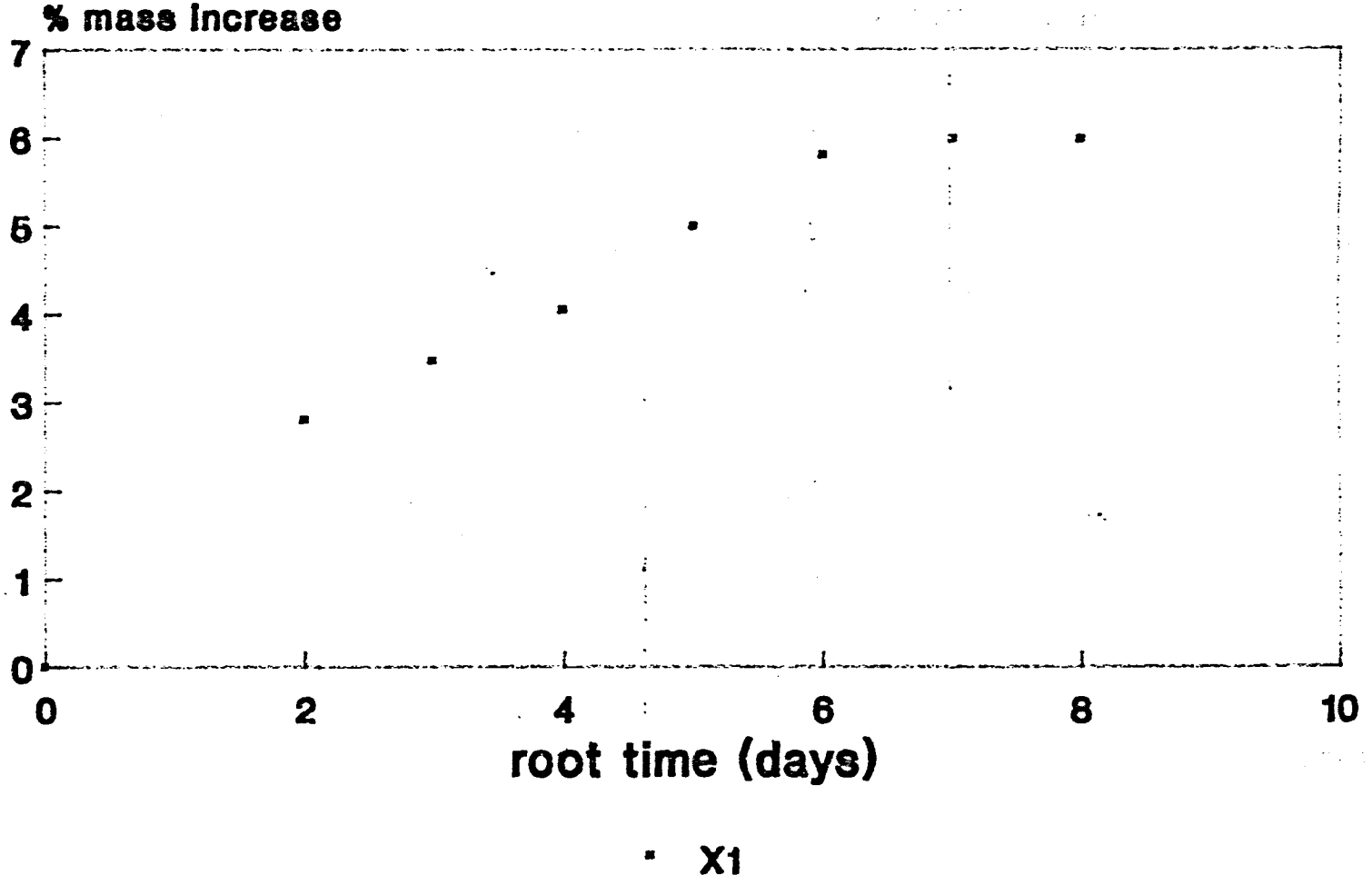


X96/2B X9

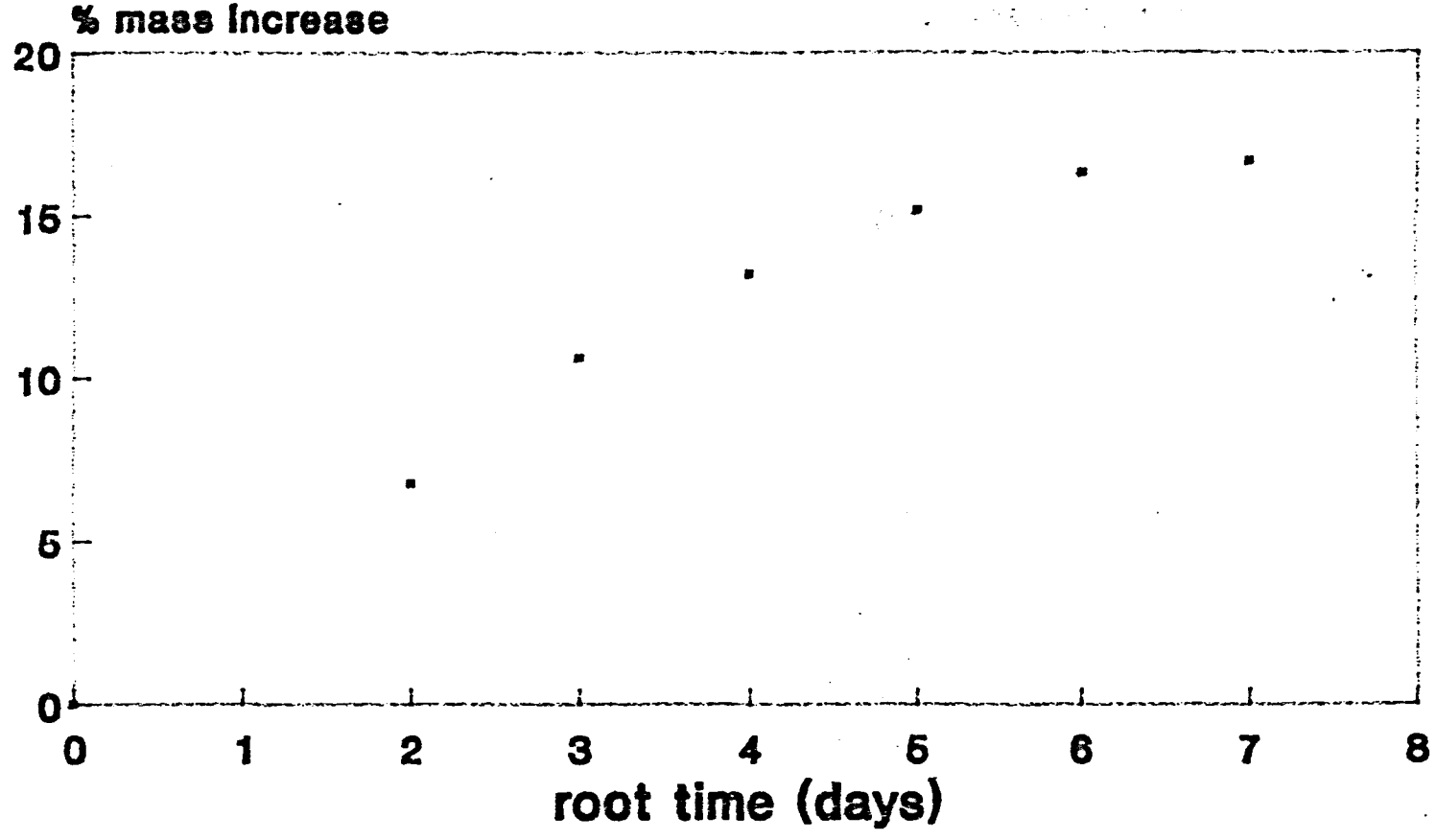

% mass increase
7
6
5
4
3
2
1
0
0
2
4
6
8
10
root time (days)
X1


% mass increase
20
15
10
5
0
0
1
2
3
4
5
6
7
8
root time (days)
100:20

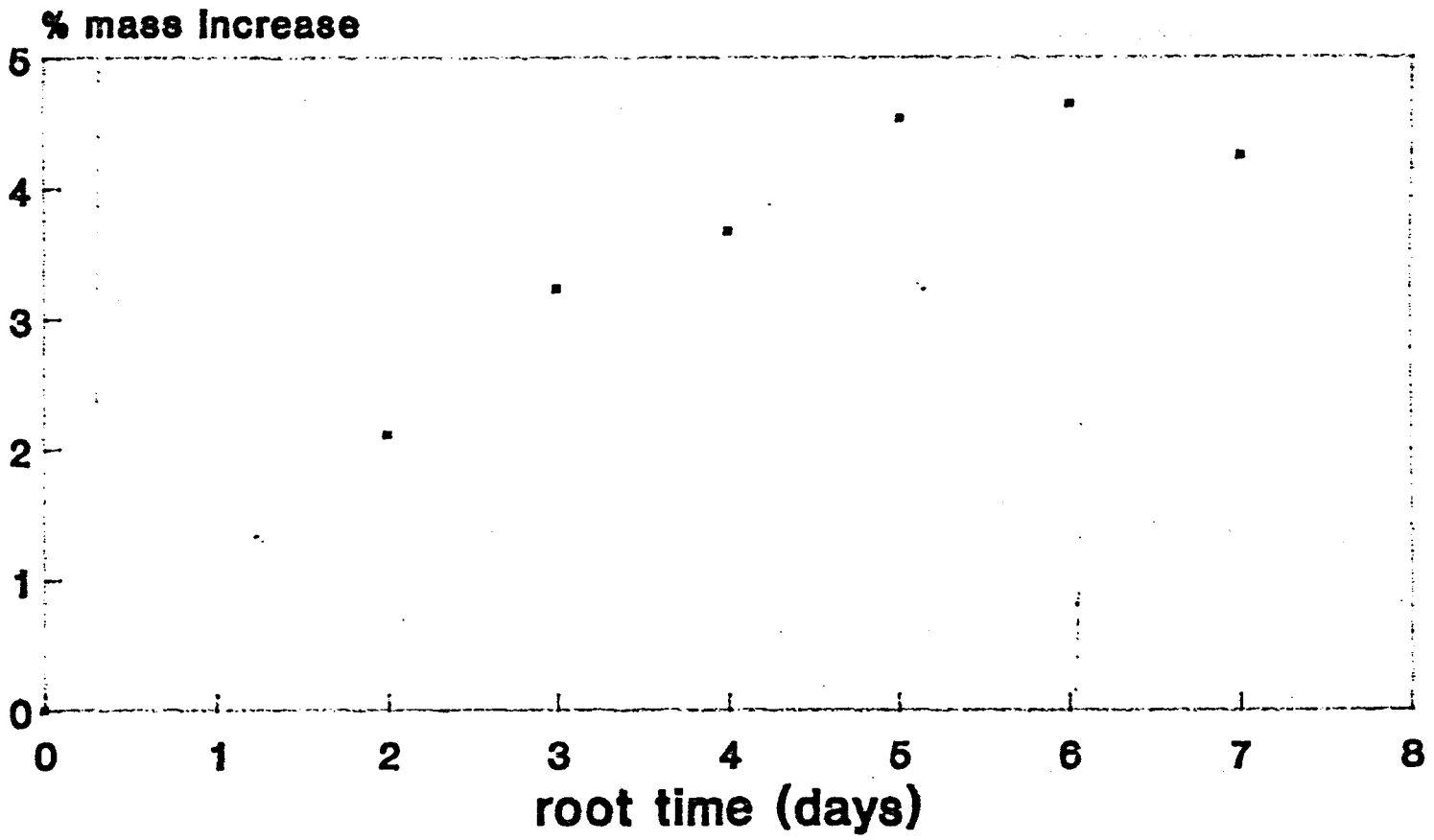
PLASTICISER MASS UPTAKE



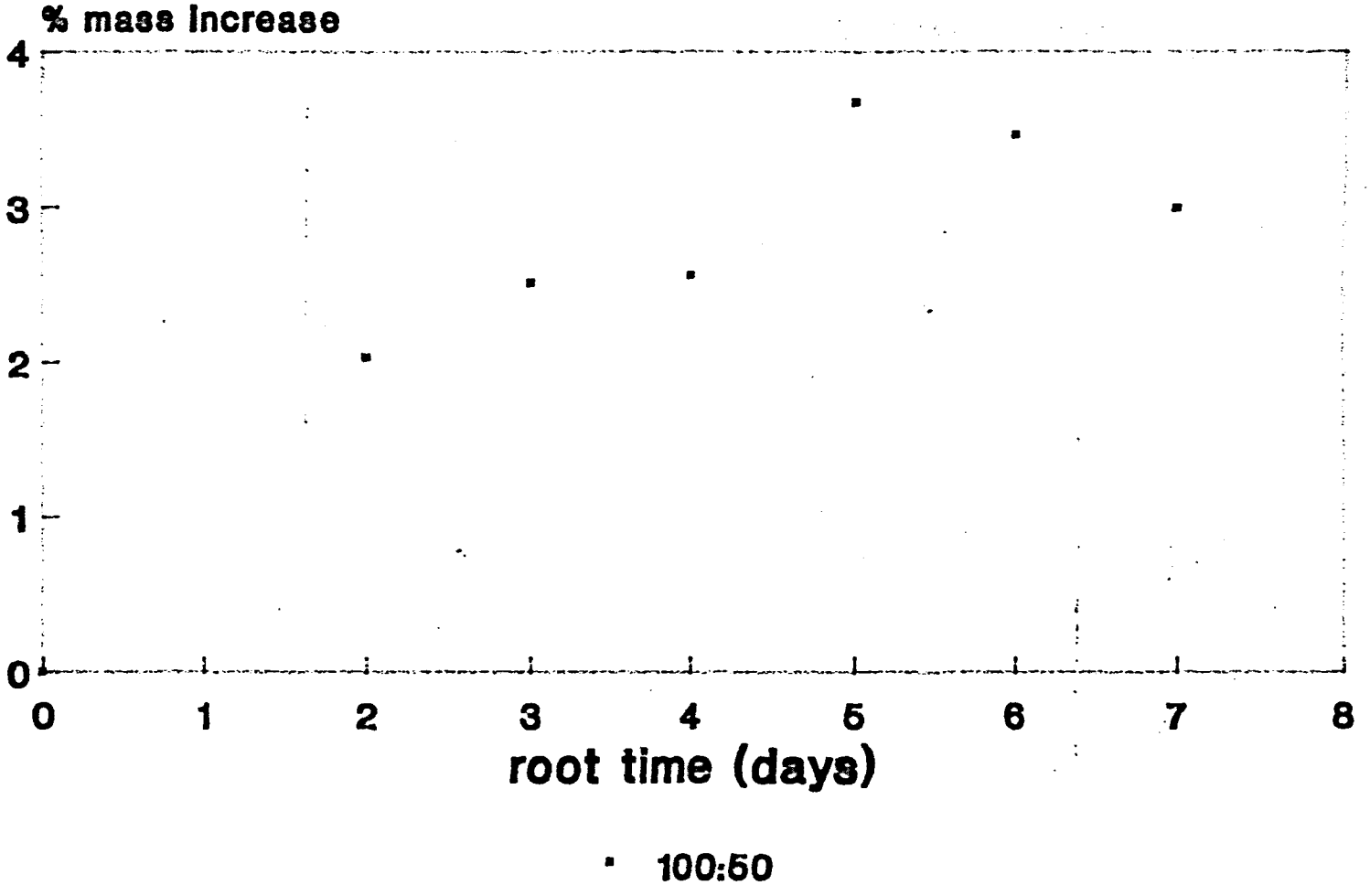
PLASTICISER MASS UPTAKE



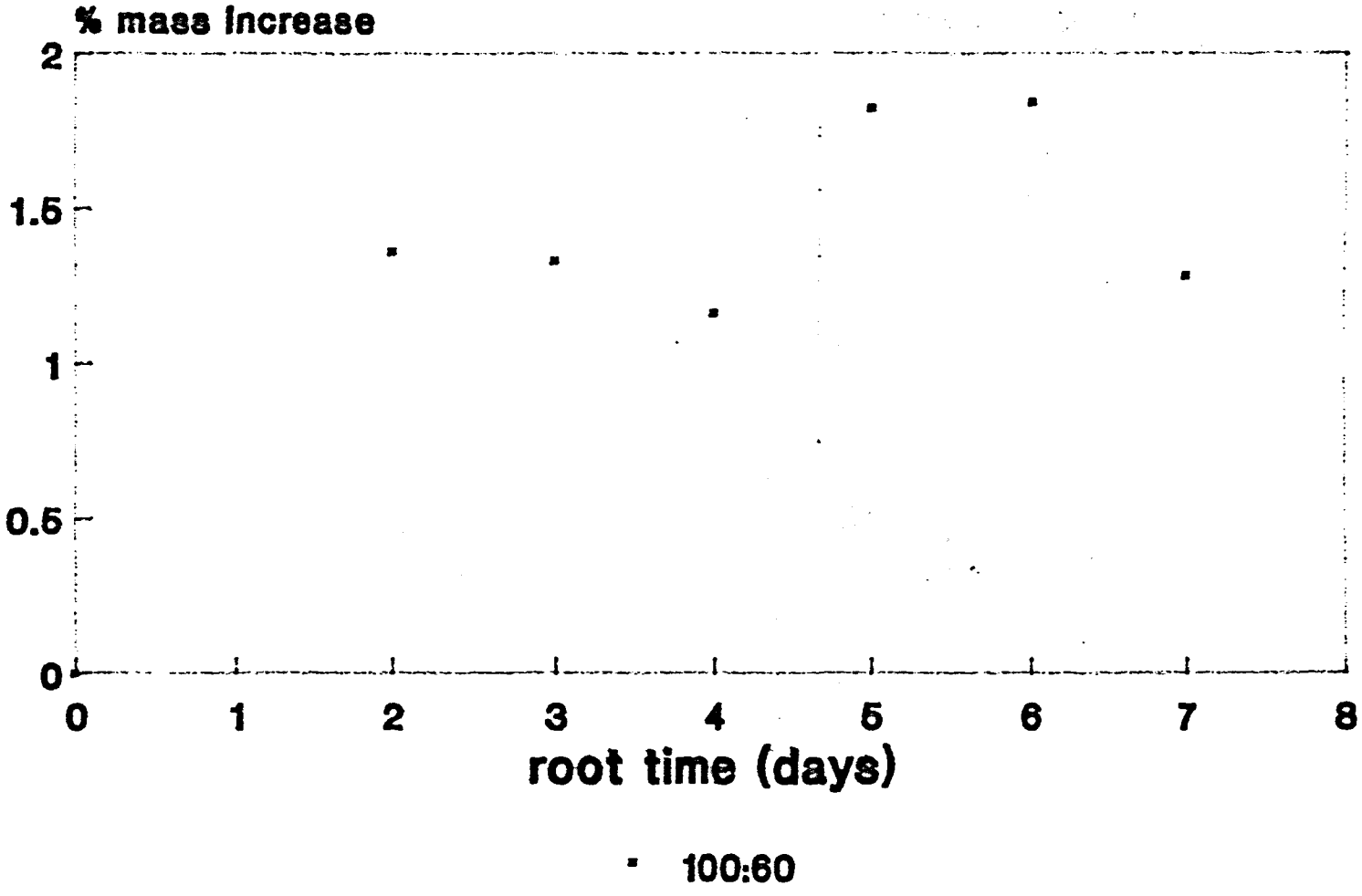
PLASTICISER MASS UPTAKE

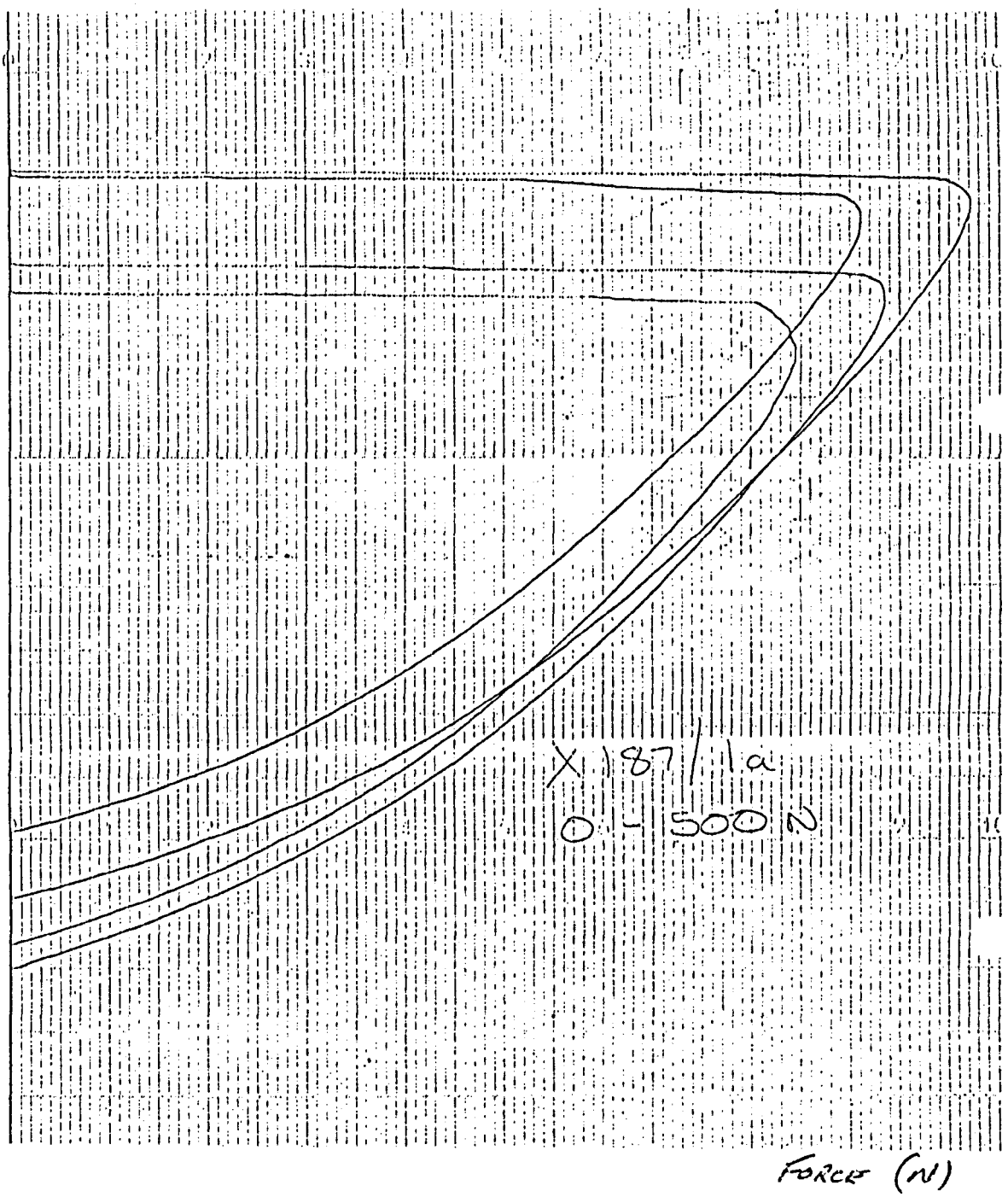


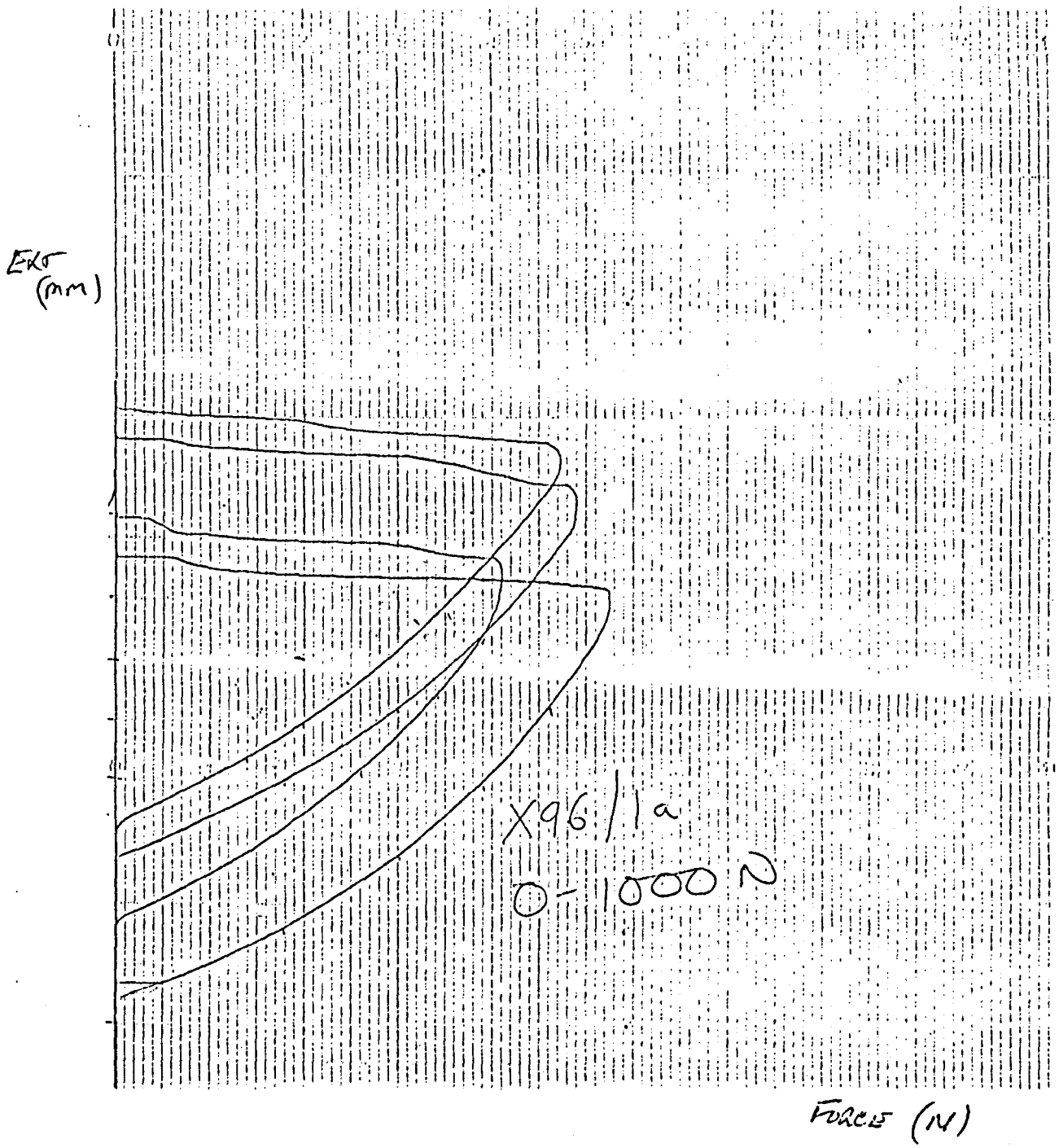
PLASTICISER MASS UPTAKE

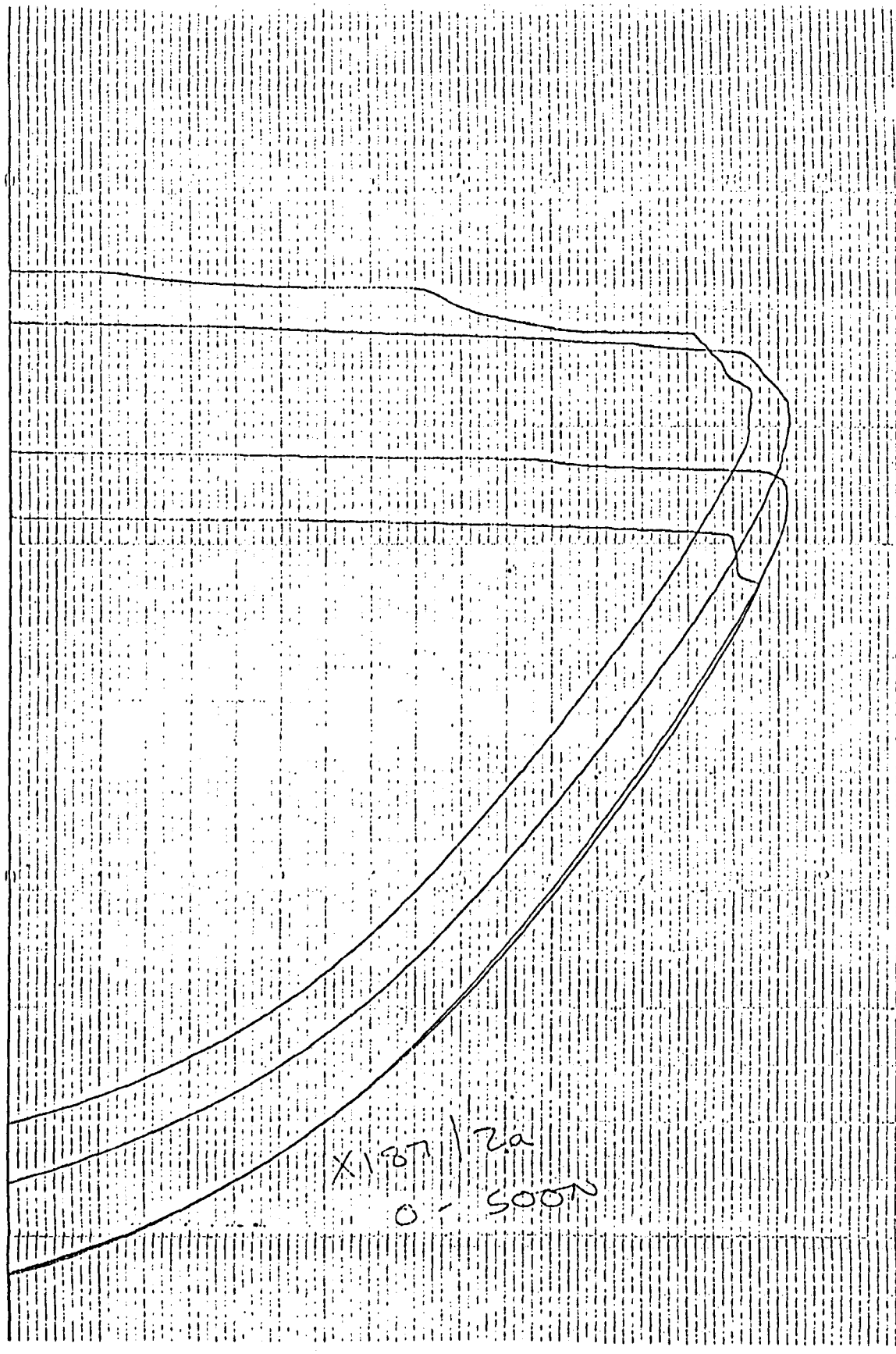


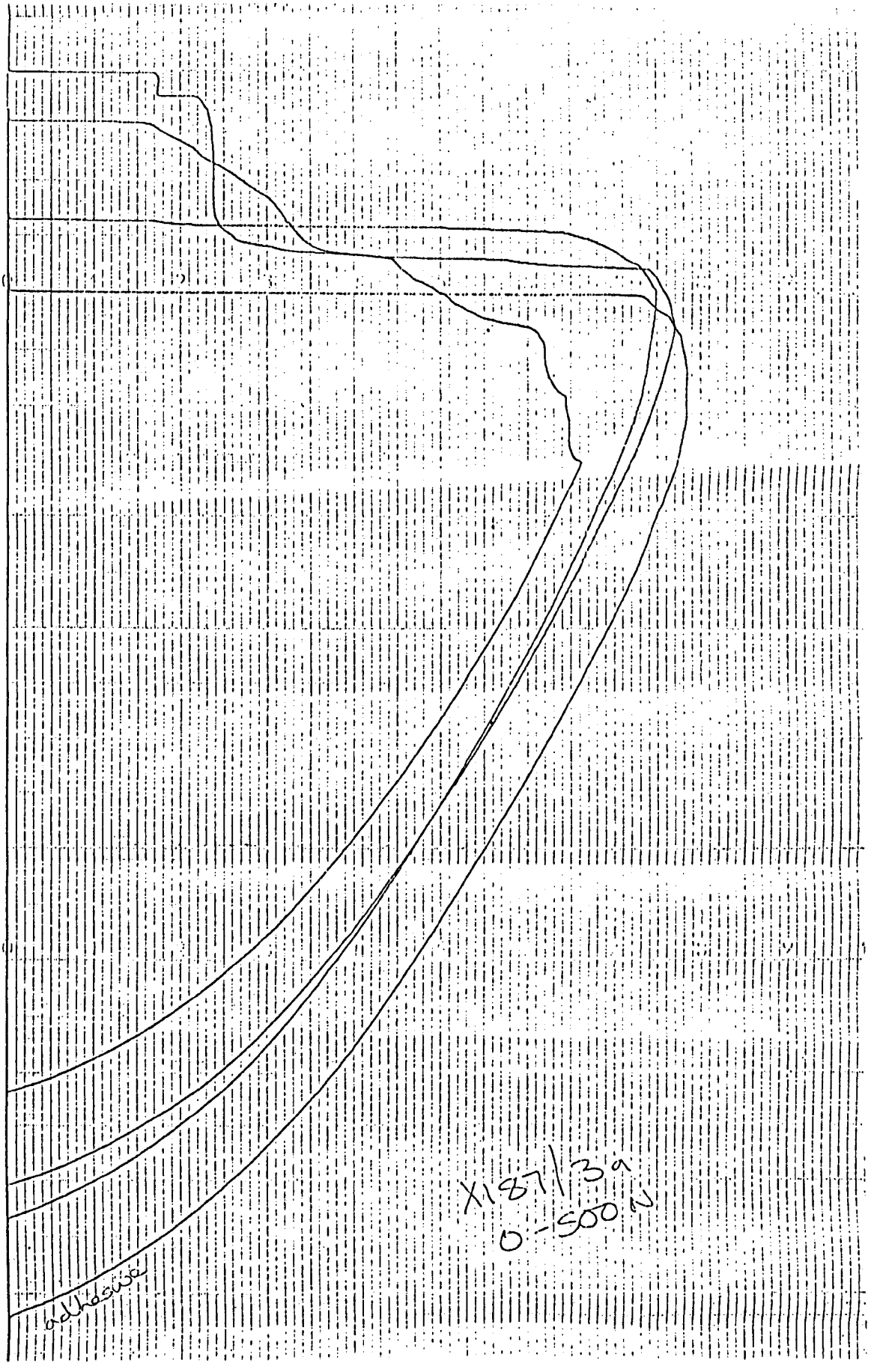
PLASTICISER MASS UPTAKE




EXT.
MM
X187/1a
0-500 N
FORCE (N)


EXT (mm)
X96/1a
0-1000 N
FORCE (N)


EXTN. (MM)
X 1207 172a
0 - 500N
FORCE (N)


EXTN
mm
X187/3a
0-500N
adhesive
FORCE (N)

ADHESION TEST RESULTS FROM GLASS-SEALNT-GLASS BONDS

FORMULATION X1

AGE	FORCE/BREAK(N)	ELONGATIONS	FORCE AT 5% EX(N)
initial	525,410,490,472 av.474/0.76	58,56,57,57 av.57	40,180,150,180 163/0/26
1 month	345,310,400,382 av.359/0.57	68,69,71,79 av.72	
2 month	370,380,340,390 av.370/0.59	61,63,67,75 av.66	110,100,130,120 av.115/0.184
3 month	300,300,305,342 av.312/0.5	50,50,53,54 av.52	110,110,105,110 av.109/0/174
4 month	305,302,265,170 av.260.5/0.417	54,33,63,30 av.44.95	120,110,100,95 av.106.25/0.17
6 month	320,176,150,195 av.210/0.34	55,36,26,53 av.42.5	95,100,105,115 av.103.75/0.166
8 month	165,127,141,182 av.154/0.245	37,33,40,42 av.38	100,85,87,88 av.90/0.144
10 month	123,125,140,95 av.121/0.19	21,43,34,25 av.30.6	75,75,75,55 av.70/0/112
12 month	100,94.5,116,113 av.106/0.17	33,26,--,50 av.36.4	
14 month	-, -, -, -,		

ADHESION TEST RESULTS FROM GLASS - SEALANT - GLASS BONDS

FORMULATION X2

AGE	FORCE AT BREAK(N)	ELONGATION%	FORCE AT 5% Ex.(N)
initial	397,442,440,485 av.441/0.71	91,86,96,87 av.90	120,120,115,110 av.116/0.186
1 month	400,360,290,320 av.342/0.548	65,63,42,50 av.55	
2 month	242,230,230,240 av.236/0/37	46,43,43,43 av.44	110,110,115,115 av.113/0.18
3 month	195,203,195,199 av.198/0.32	33,38,40,38 av.37	110,100,100,105 av.104/0.166
4 month	248,185,172,217 av.205.5/0.33	60,33,57,60 av.52.5	110,95,95,105 av.101.25/0.162
6 month	165,215,170,192 av.185.5/0.29	37,40,39,41 av.39.4	100,95,90,75 av.90/0.144
8 month	137,130,132,138 av.134/0.22	40,37,33,35 av.36.25	68,85,85,80 av.80/0.127
10 month	127,130,133,96 av.122/0.19	30,42,29,36 av.34.2	60,50,75,55 av.60/0.096
12 month	97,114,164,144 av.130/0.21	53,54,46,42 av.48.8	
14 month	-, -, -, -,		

ADHESION TEST RESULTS FROM GLASS - SEALANT - GLASS BONDS

FORMULATION X3

AGE	FORCE/BREAK(N)	ELONGATION	FORCE at 5% EX(N)
initi al	415,430,430,410 av.421/0.675	108,118,123, av.118	105,95,105,105 av.102/0.164
1 month	255,248,362,390 av.314/0.502	41,50,53,63 av.52	
2 month	160,142,151,380 av.151/0.24	21,25,21,58 av.22	130,110,130,130 av.125/0.2
3 month	156,175,175,205 av.178/0.285	42,42,27,33 av.36	95,75,110,120 av.100/0.16
4 month	155,164,153,220 av.173/0.28	17,27,22,27 av.23.35	105,102,105,102 av.103.5/0.17
6 month	95,150,135,135 av.129/0.21	40,42,38,33 av.38.1	70,105,90,70 av.83.25/0.134
8 month	132,140,208,124 av.151/0.24	40,30,53,37 av.40	85,95,75,82.5 av.84.375/0.135
10 month	93,124,140,115 av.118/0.19	34,34,36,42 av.36.5	50,80,80,70 av.70/0.112
12 month	95,35,75,76 av.70.1/0.11	31,21,38,28 av.29.35	
14 month	-, -, -, -,		

ADHESION TEST RESULTS FROM GLASS - SEALANT - GLASS BONDS

FORMULATION X4

AGE	FORCE/BREAK(N)	ELONGATION	FORCE at5%EX(N)
initi al	392,385,375,330 av.371/0.593	153,149,142,146 av.147	85,85,85,80 av.84/0.134
1 month	170,330,210,95 av.201/0.322	28,46,33,8.3 av.27	
2 month	105,95,115,130 av.111/0	8.3,9.2,8.2,10 av.9	100, -, -,120 av.110/0.176
3 month	92,206,160,135 av.148/0.23	11,38,18,12.5 av.20	90,100,100,100 av.97.5/0.156
4 month	124,100,55,222 av.125/0.20	7,6,5,30 av.12	105,100, -, 110 av.105/0.17
6 month	53,45,187,38 av.80/0.13	8,8,36,6 av.14.35	-, -, 110, - 110/0.176
8 month	All bonds failed adhesively before test.		
10 month	All bonds failed adhesively before test.		

ADHESION TEST RESULTS FROM GLASS - SEALANT - GLASS BONDS

FORMULATION X7

AGE	FORCE/BREAK(N)	ELONGATION	FORCE at 5%EX(N)
initial	360,380,365,368 av.368/0.59	100,112,102,119 av.108	86,90,90,90 av.88/0.14
1 month	376,350,290,265 av.320/0.51	67,54,54,53 av.57	130,120,120,110 av.120/0.192
2 month	210,195,310,225 av.235/0.376	37.5,33,50,53.3 av.43.5	120,80,105,'00 av.101/0.162
3 month	190,250,265,185 av.222/0.36	33,45,46.42 av.41.4	110,120,120,110 av.115/0.184
4 month	220,245,164,166 av.188/0.32	54,60,37,39 av.48	90,90,80,80 av.85/0.136
6 month	172,160,138,158 av.157/0.25	32,32,32,32 av.32	95,90,100,95 av.95/0.152
8month	138,130,126,130 av.131/0.21	27,29,48,35 av.35	70,65,60,75 av.67.5/0.108
10 month	160,135,90,104 av.122.25/0.20	44,40,33,28 av.36.25	
12 month	118,98,115,144 av.118.75/0.19	23,42,21,35 av.30.2	80,60,68,62 av.67.5/0.108
14 month	160,152,126,151 av.147/0.235	40,21,33,27 av.30.2	

ADHESION TEST RESULTS FROM GLASS-SEALANT-GLASS BONDS

FORMULATION X8

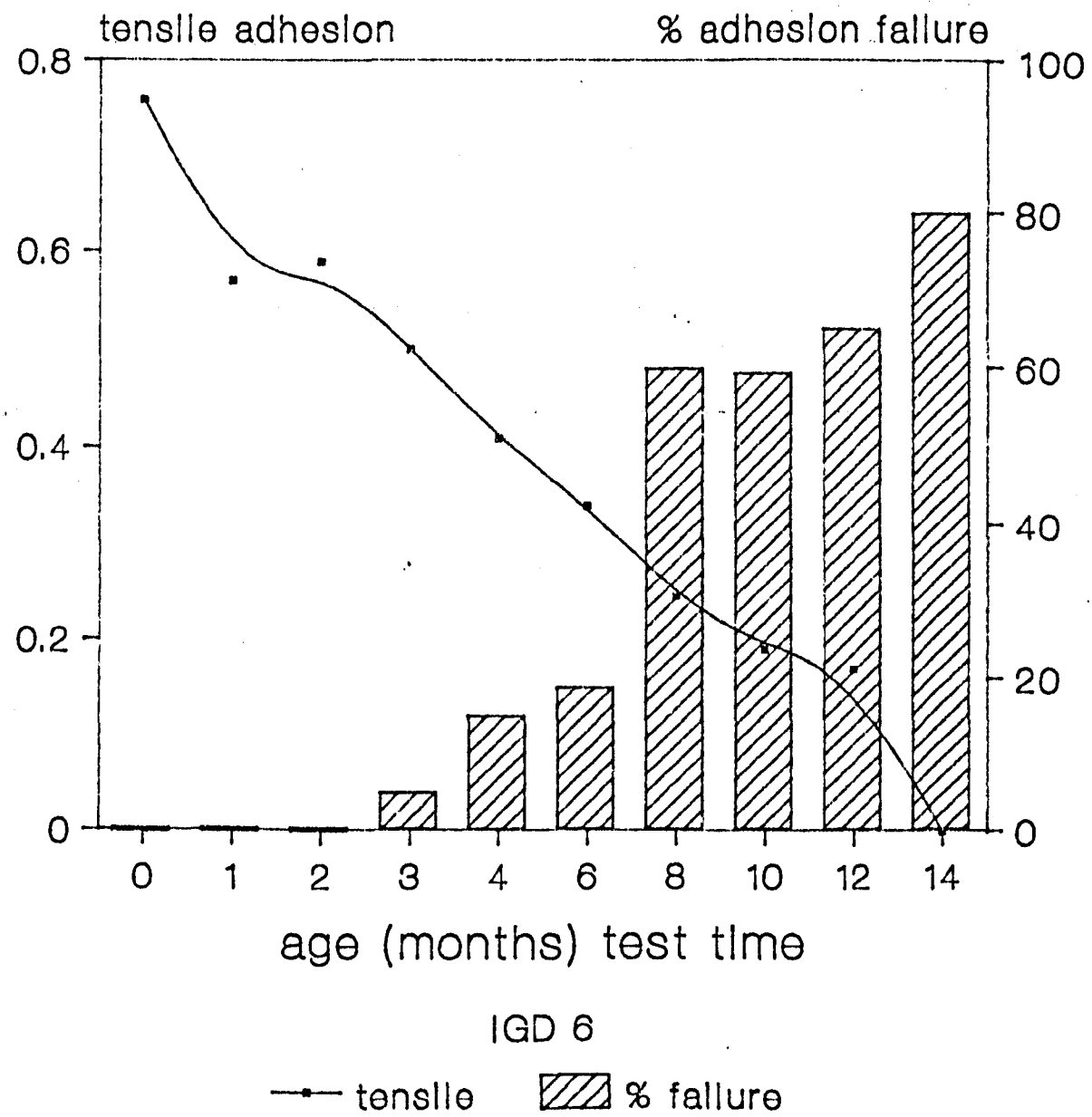
AGE	FORCE/BREAK(N)	ELONGATION	FORCE AT 5% EX (N)
initial	360,380,390,340 av.367/0.588	126,134,144,120 av.131	85,80,85,80 av.83/
1 month	345,340,347,240 av.344/0.55	48,48,51,35 av.46	125,130,130,120 av.126/0/20
2 month	210,188,180,285 av.216/0.345	33,22.5,26.7,50 av.33.125	120,120,120,115 av.119/0.19
3 month	210,180,170,292 av.213/0.34	36,33,34,52 av.38.7	115,105,110,115 av.111/0.178
4 month	285,142,127,140 av.174/0.28	47,30,26,24 av.32	110,100,100,105 av.104/0.166
6 month	126,162,112,136 av.134/0.134	22,17,25,20 av.21.05	115,75,107,95 av.98.125/0.157
8 month	222,180,207,200 av.202.25/0.32	39,39,42,40 av.39.8	110,95,100,105 av.102.5/0.164
10 month	88.90,120,85 av.95.75/0,15	30,30,21,25 av.26.25	
12 month	86,79,81,88 av.83.5/0.135	19,17,19,13 av.16.9	62,60,62,70 av.63.5/0.1016
14 month	193,78,138,96 av.126/0.20	38,25,18,28 av.27.3	

ADHESION TEST RESULTS FROM GLASS-SEALANT-GLASS BONDS

FORMULATION X9

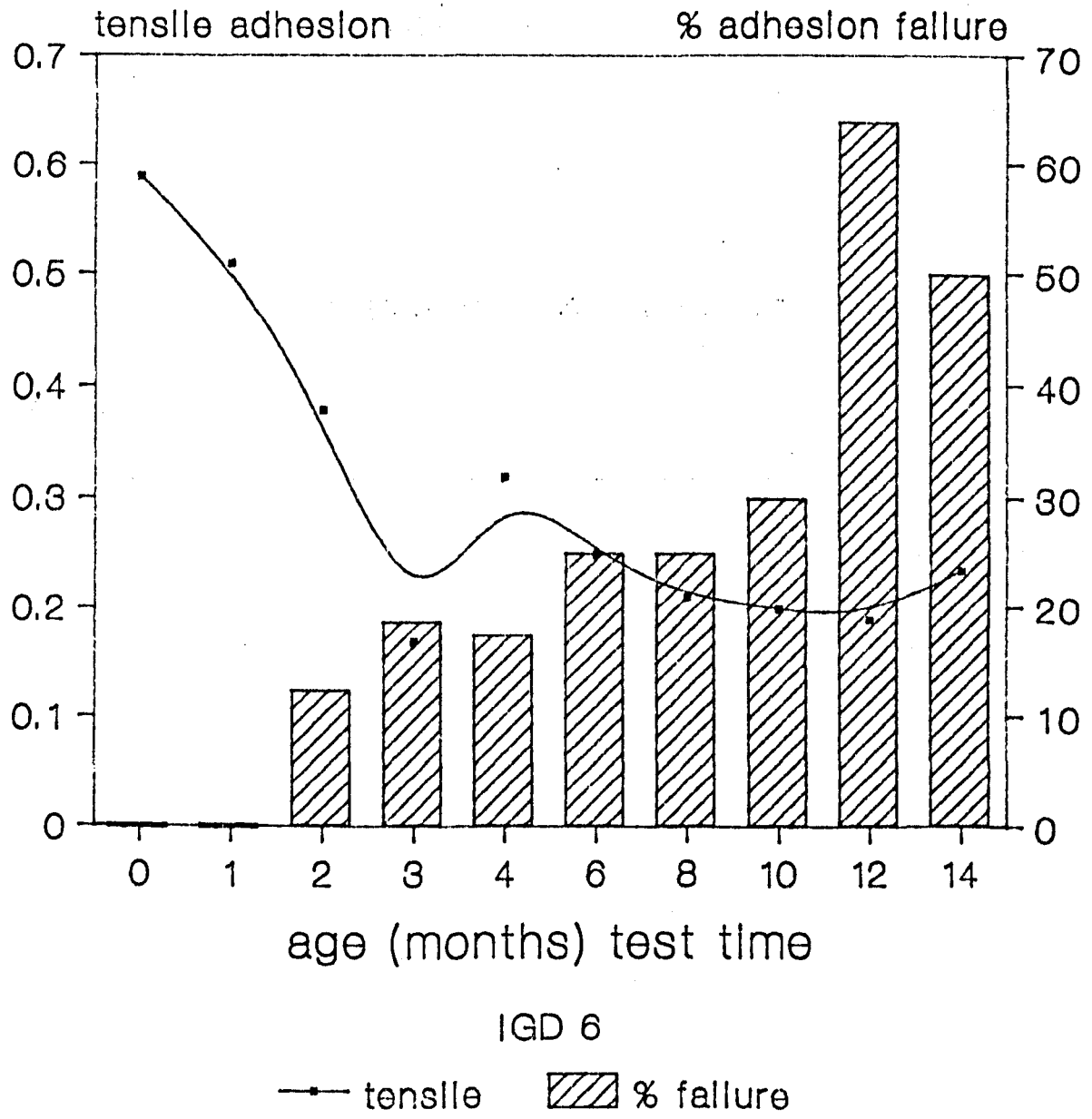
AGE	FORCE/BREAK(N)	ELONGATION	FORCE AT 5% EX (N)
initial	165,160,120,110 av.139/0.222	137,148,157,150 av.148	45,45,45,45 av.45/0.072
1 month	222,195,181,190 av.297/0.31	67,62,53,62 av.61	70,70,65,70 av.69/0.11
2 month	185,152,150,145 av.158/0.258	63,56,58,54 av.58	60,65,55,55 av.59/0.094
3 month	136,140,166,160 av.151/0.24	56,53,57,61 av.56.6	60,65,65,60 av.62.5/0.1
4 month	115,130,168,115 av.132/0.17	55,55,67,50 av.57	45,50,55,50 av.50/0.08
6 month	100,99,115,100 av.103.5/0.165	63,53,58,55 av.57.7	45,45,40,40 av.42.5/0.068
8 month	80,77,85,90 av.83/0.13	58,50,57,55 av.55.2	37,35,38,40 av.37.5/0.06
10 month	62,57,80,73 av.68/0.11	50,--,52,54 av.51.9	
12 month	66,72,68,68 av.68.5/0.11	46,46,42,50 av.45.9	34,38,34,34 av.35/0.056
14 month	45,55,65,55 av.55/0.08	42,39,43,50 av.43.55	

ADHESION BREAKDOWN
HIGH HUMIDITY TEST



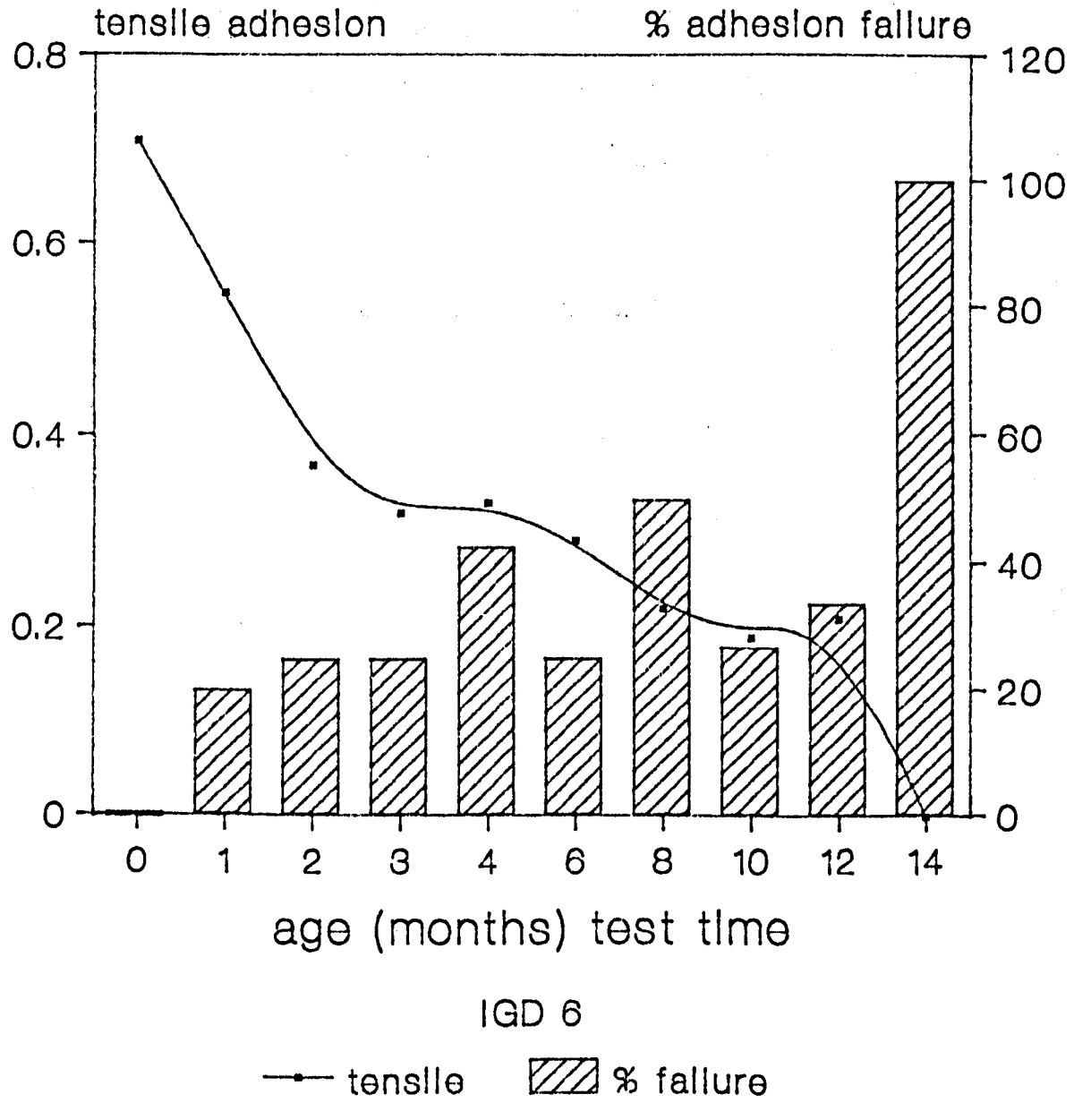
X96/1A

ADHESION BREAKDOWN
HIGH HUMIDITY TEST



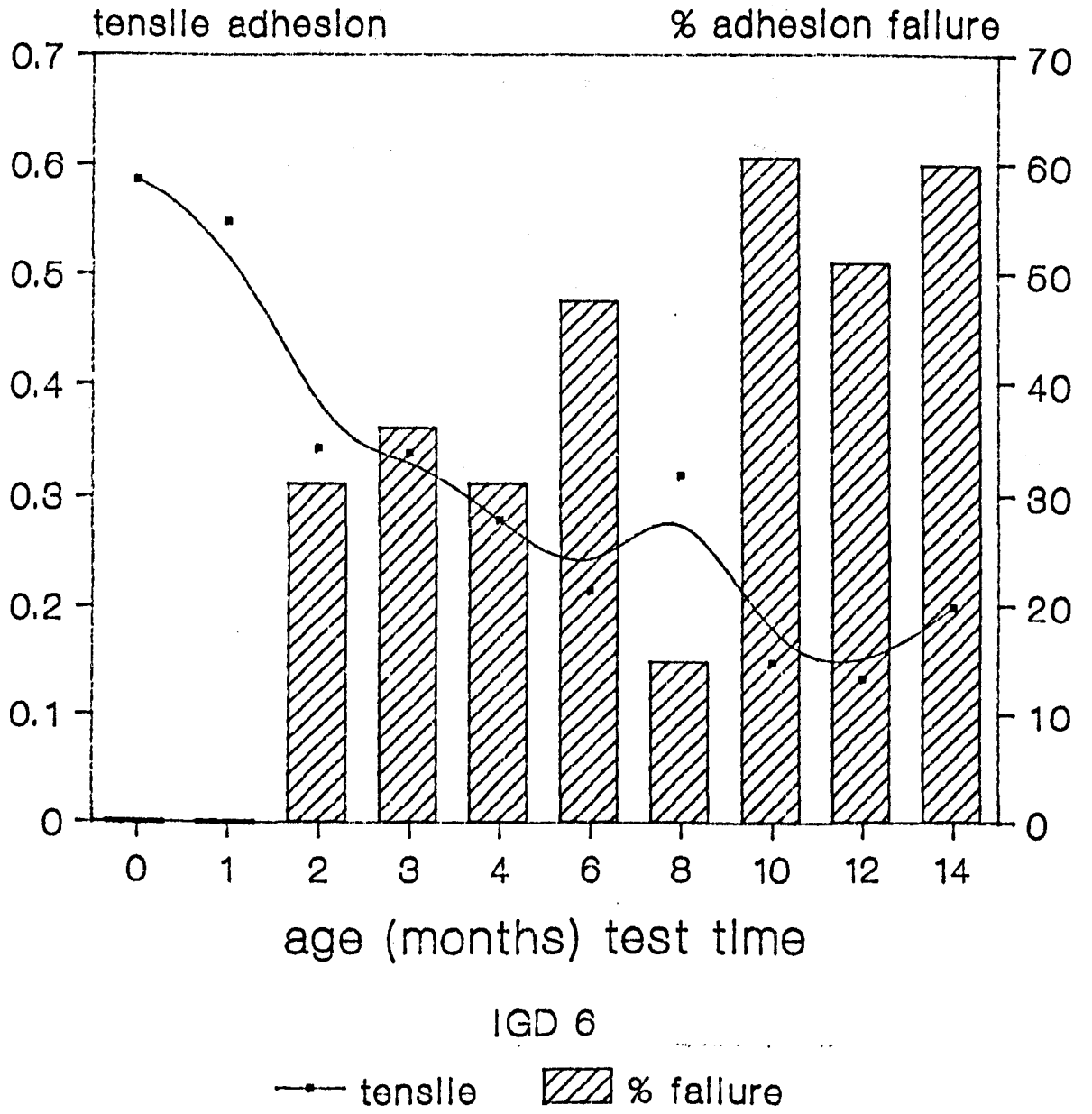
X96/2A

ADHESION BREAKDOWN
HIGH HUMIDITY TEST



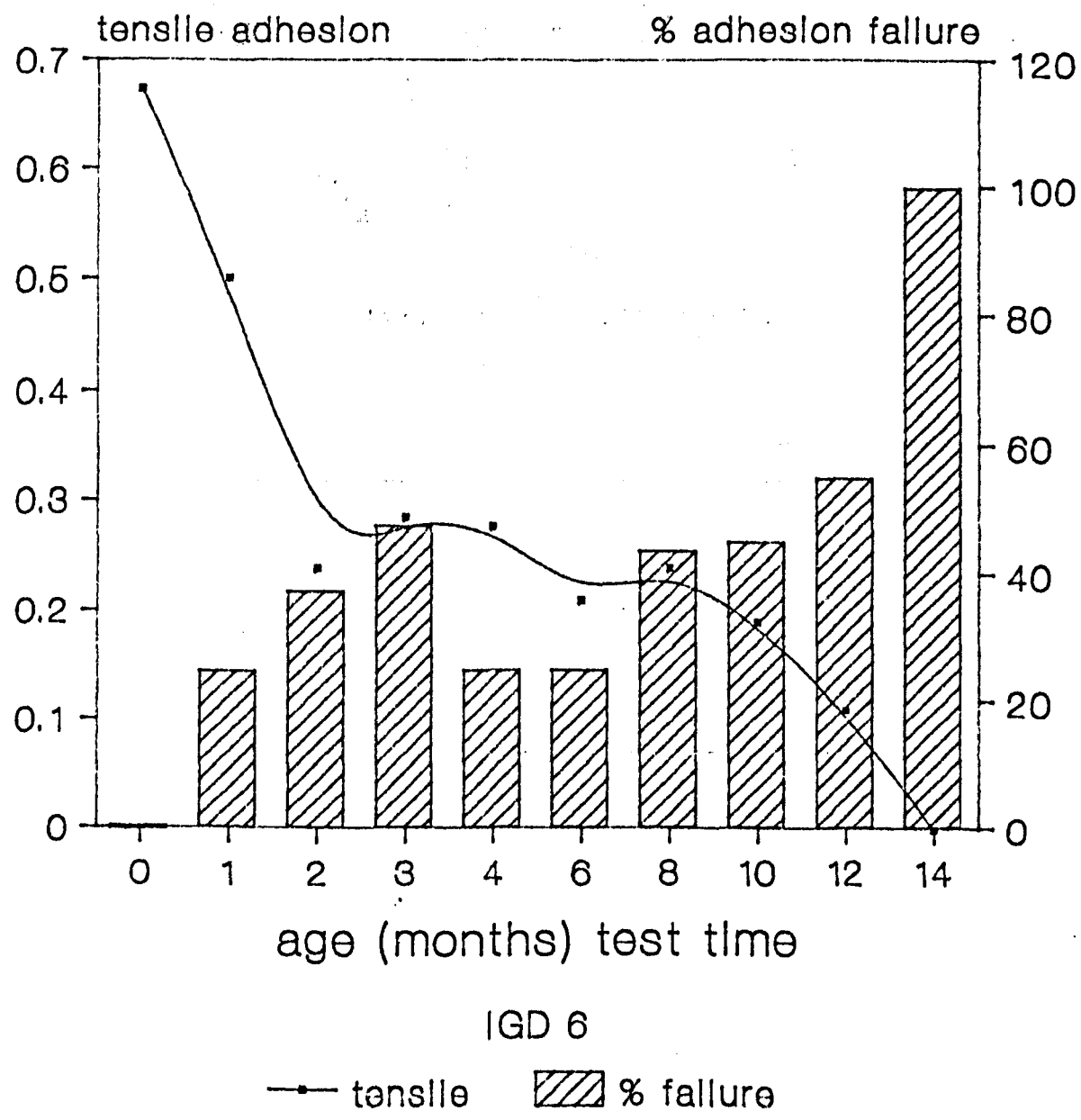
X187/1A

ADHESION BREAKDOWN
HIGH HUMIDITY TEST



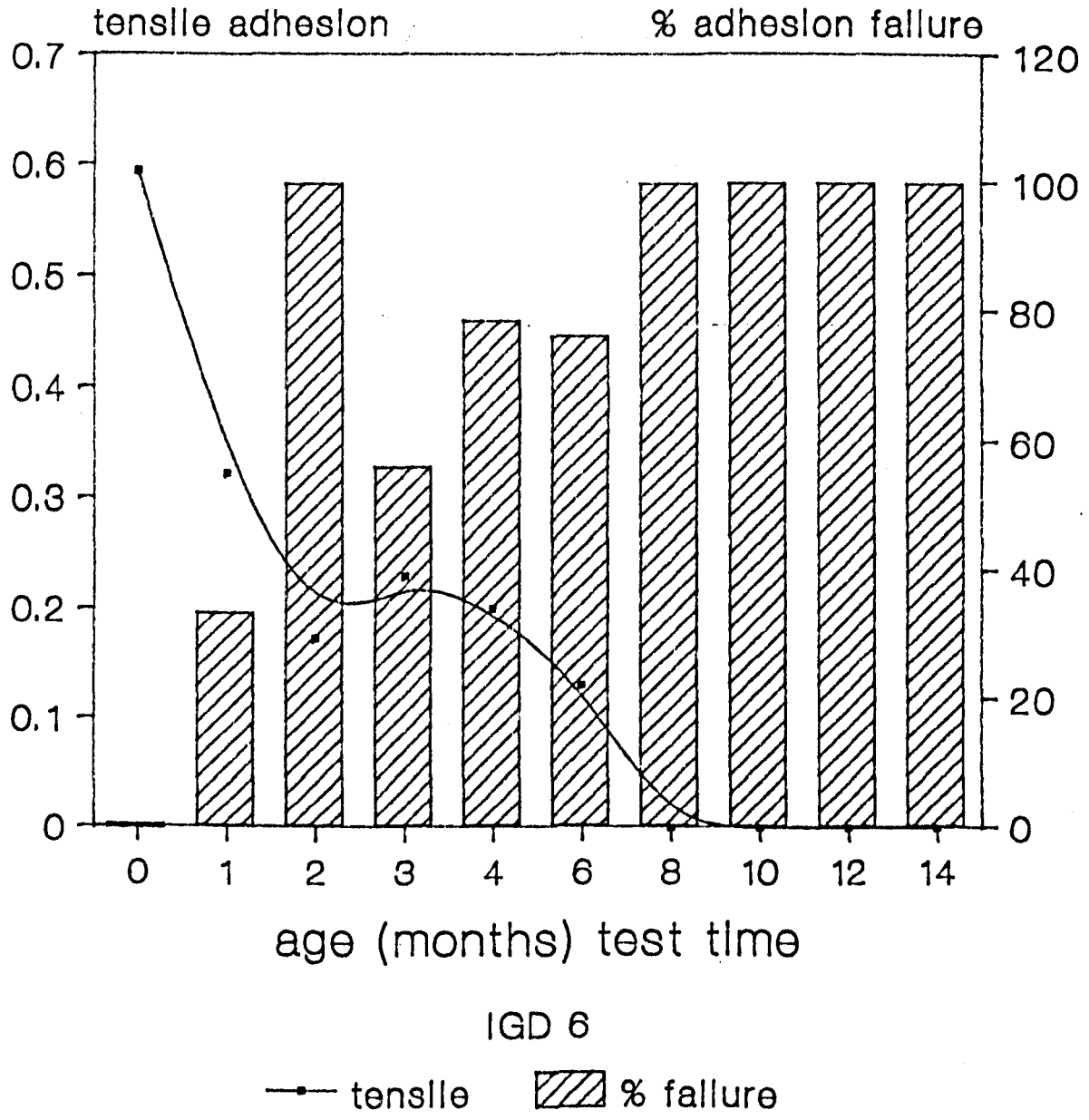
X96/3A

ADHESION BREAKDOWN
HIGH HUMIDITY TEST



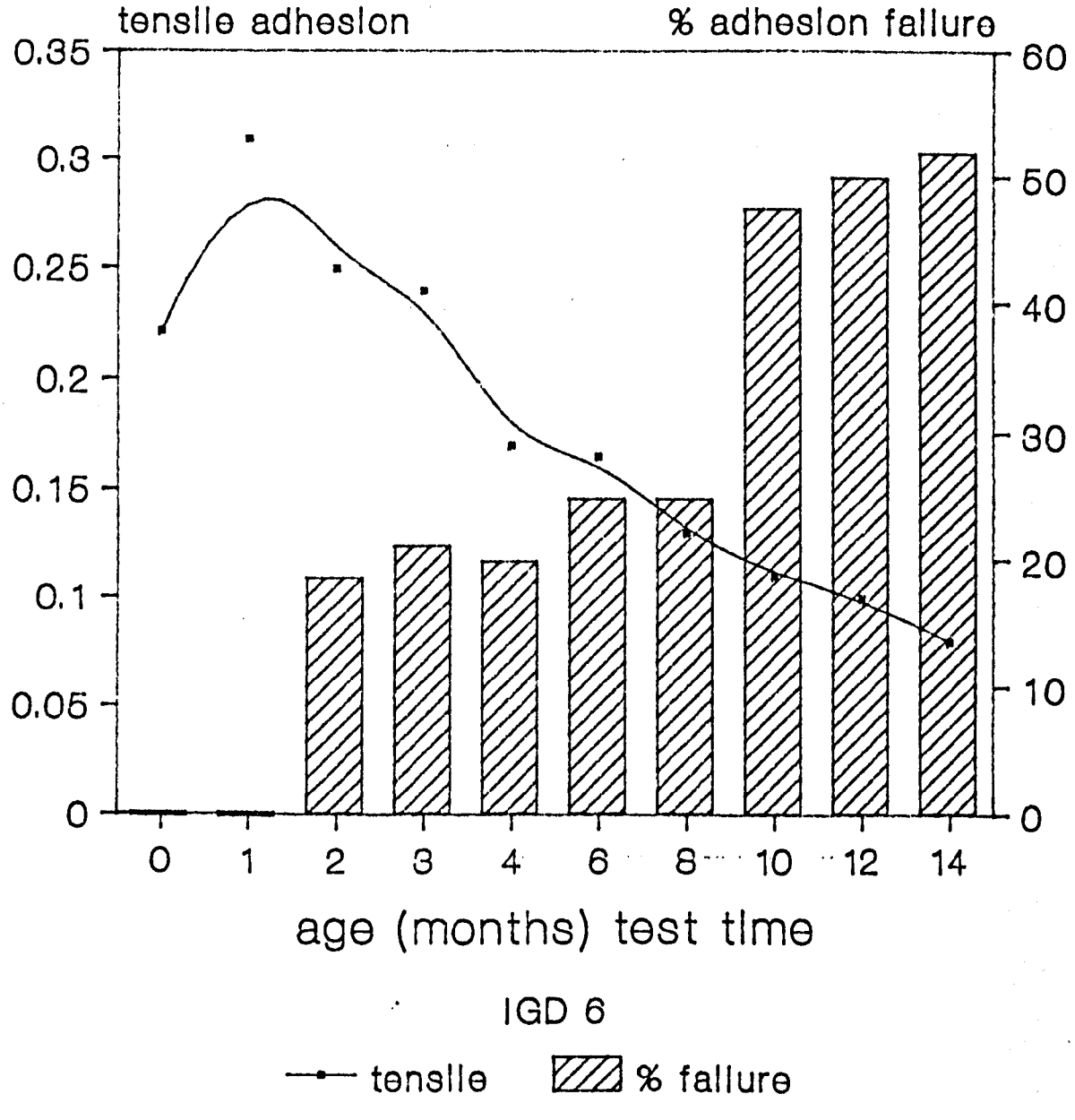
X187/2A

ADHESION BREAKDOWN
HIGH HUMIDITY TEST



X187/3A

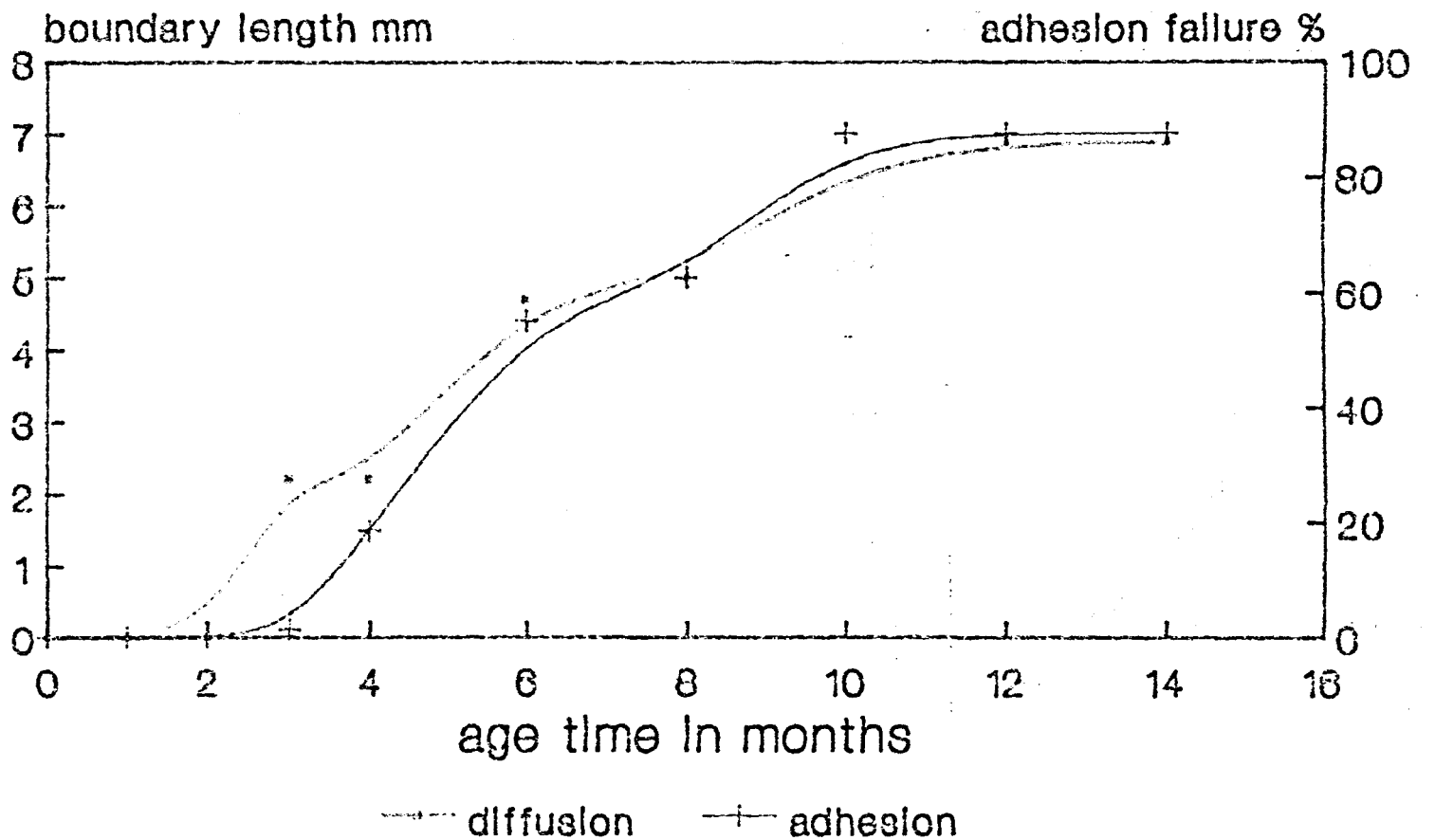
ADHESION BREAKDOWN
HIGH HUMIDITY TEST



X96/2B

RATE OF BOUNDARY CHANGE

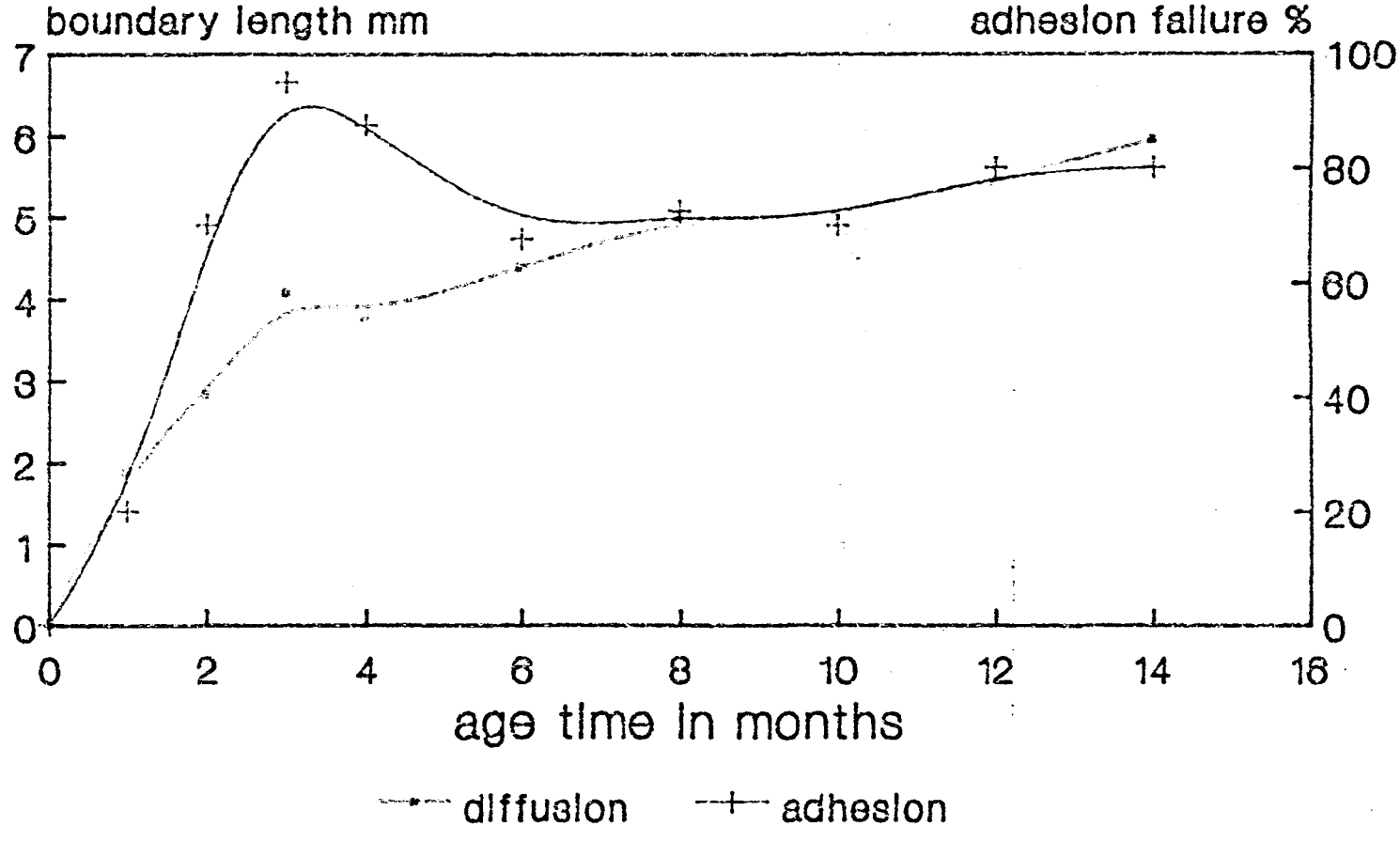
against adhesion loss



X98/1A

RATE OF BOUNDARY CHANGE

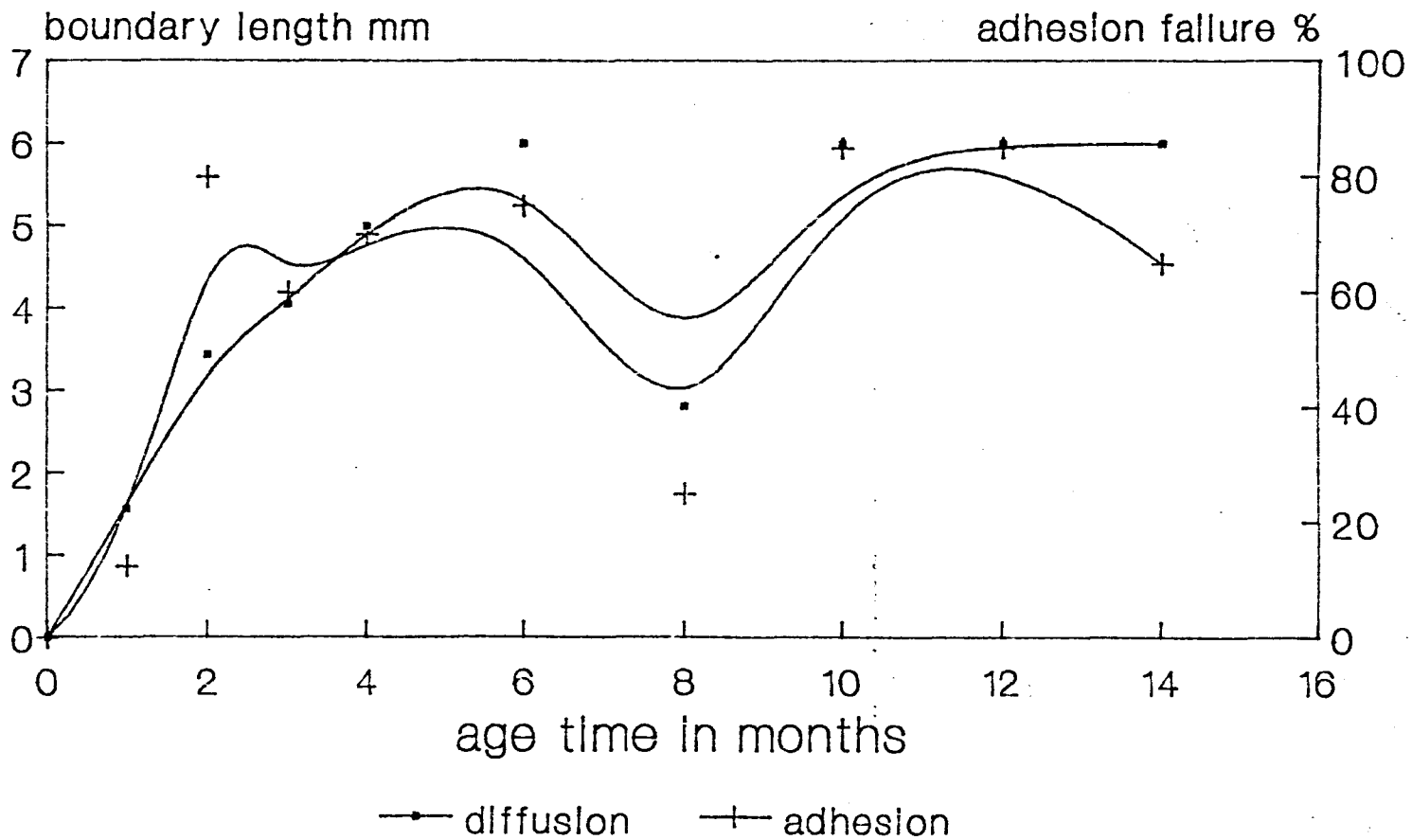
against adhesion loss



X187/2A

RATE OF BOUNDARY CHANGE

against adhesion loss

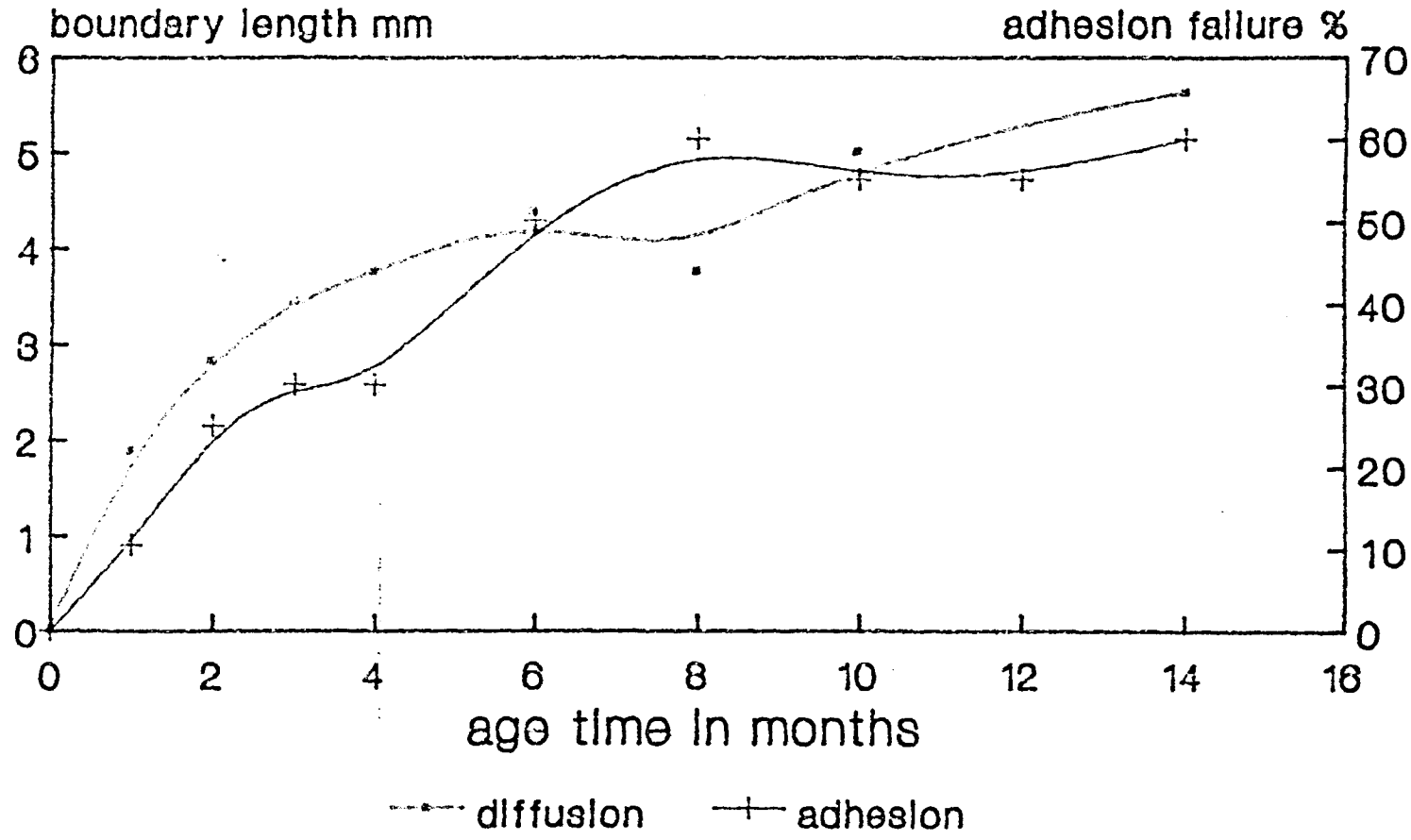


263

X96/3A

RATE OF BOUNDARY CHANGE

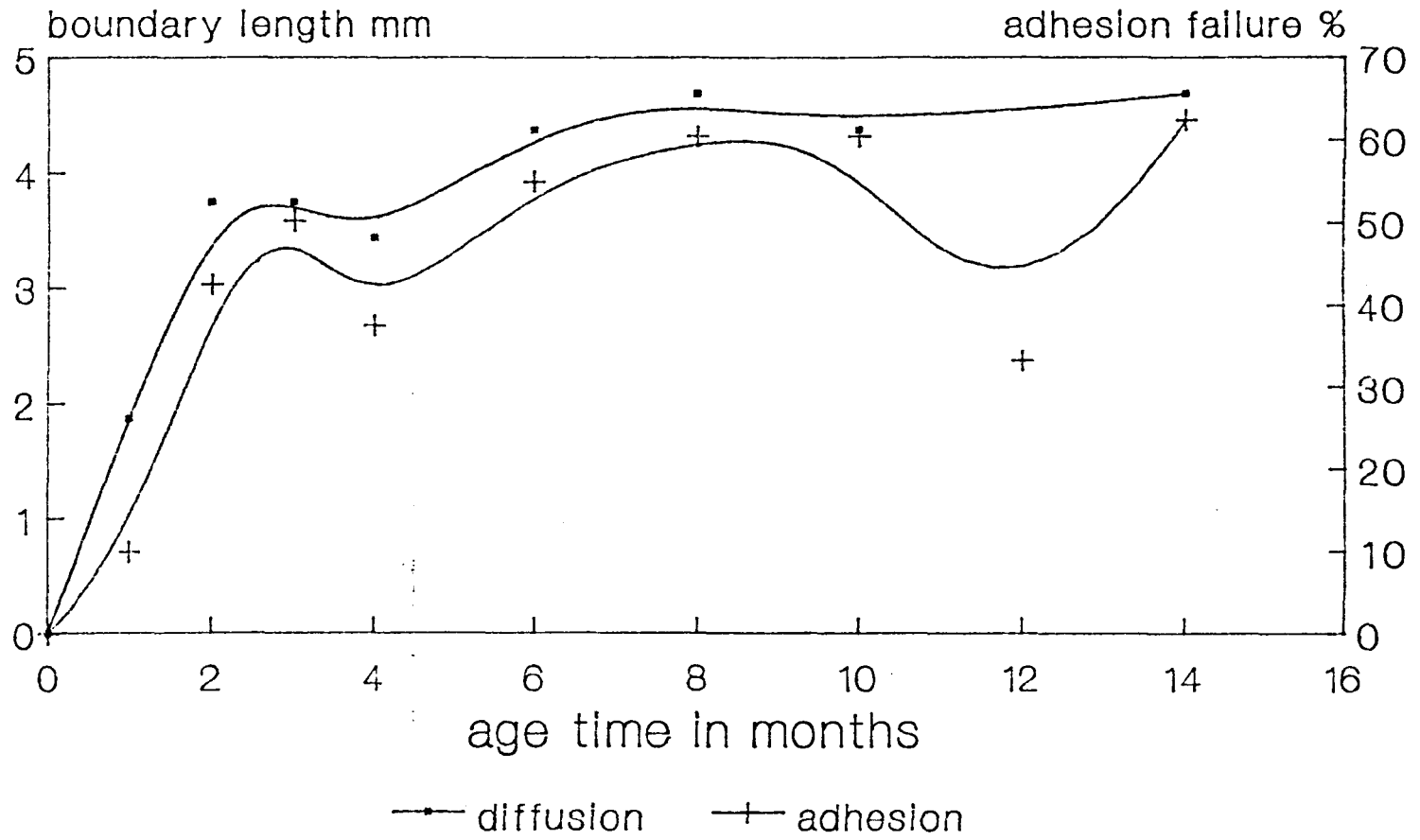
against adhesion loss



X96/2A

RATE OF BOUNDARY CHANGE

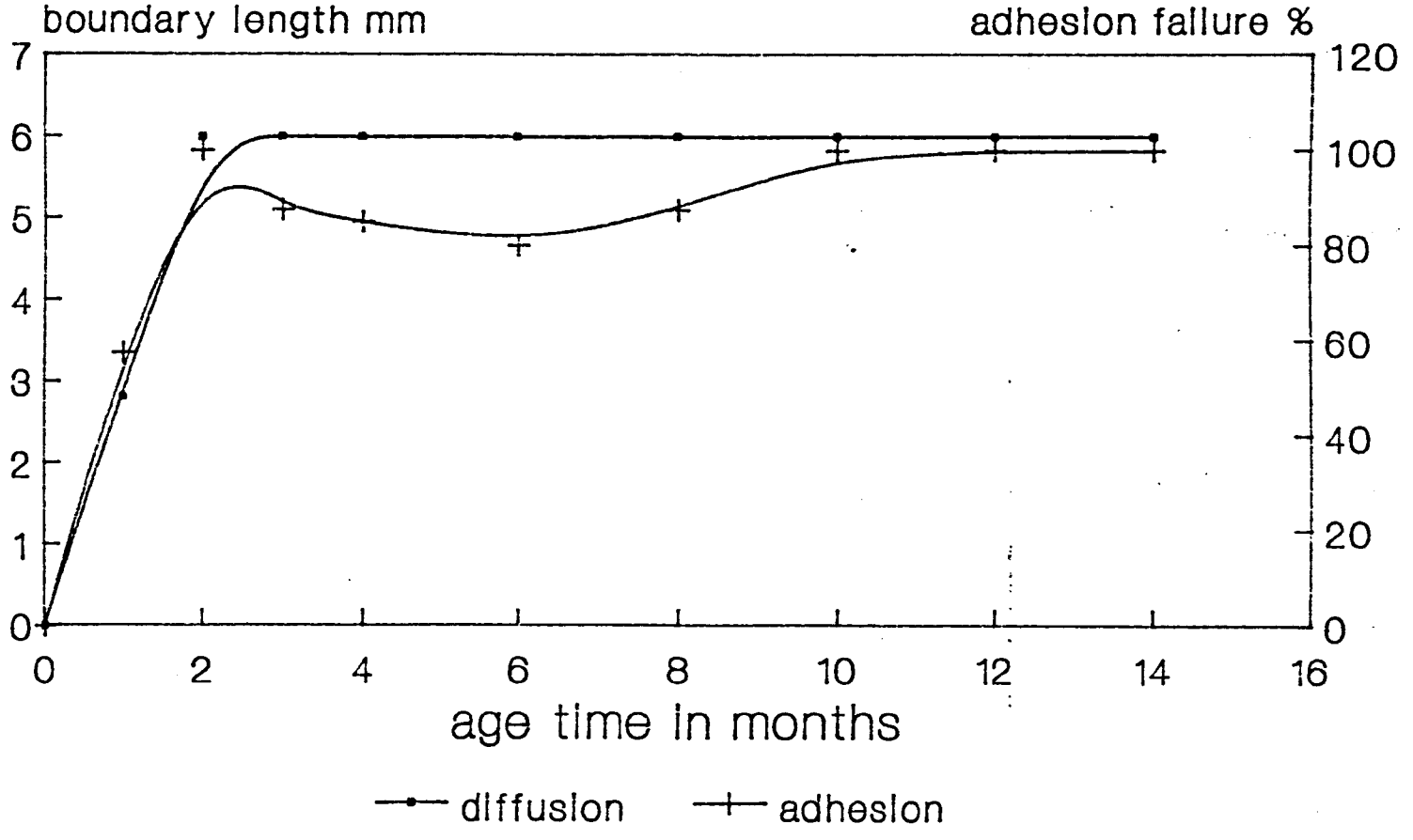
against adhesion loss



X187/1A

RATE OF BOUNDARY CHANGE

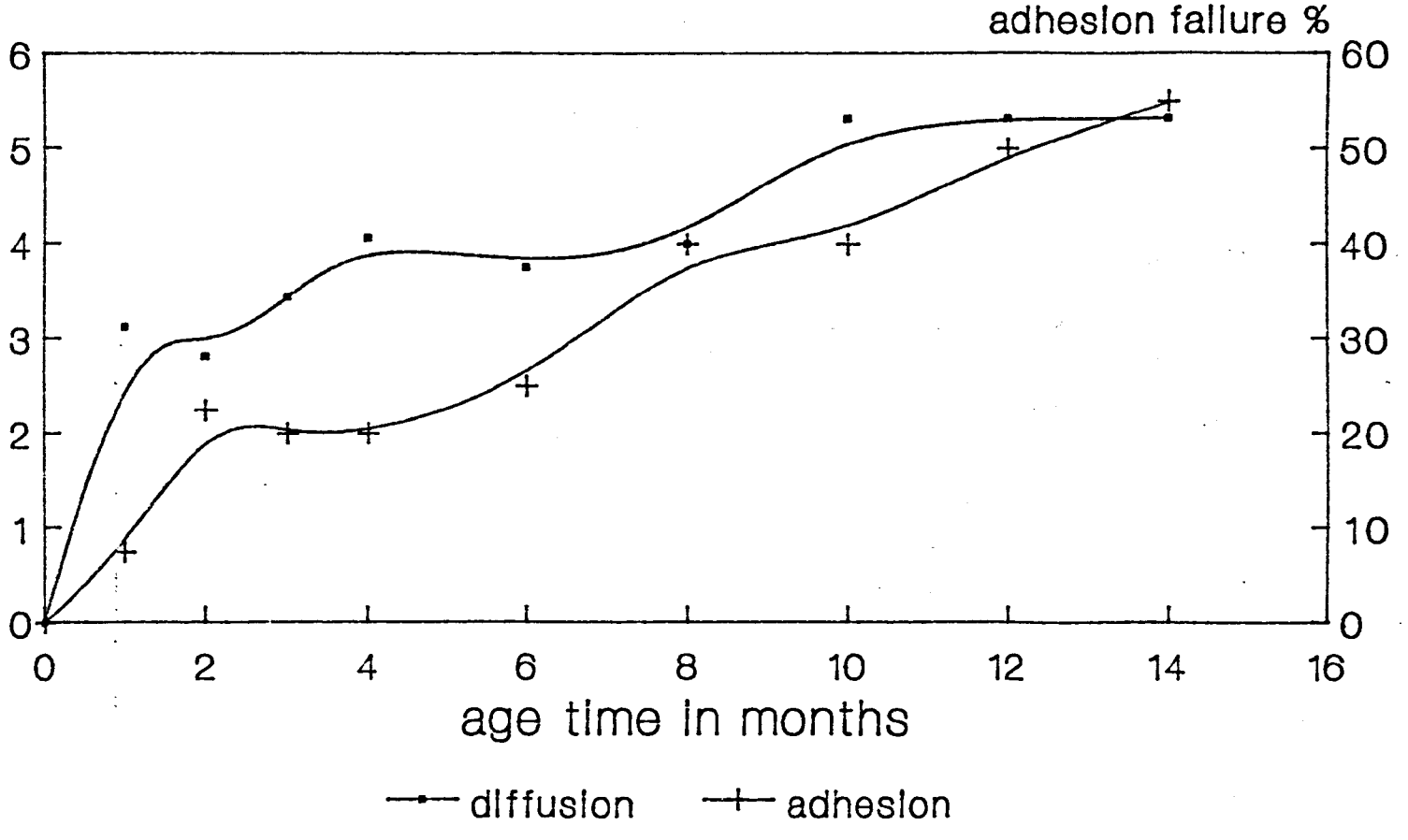
against adhesion loss



X187/3A

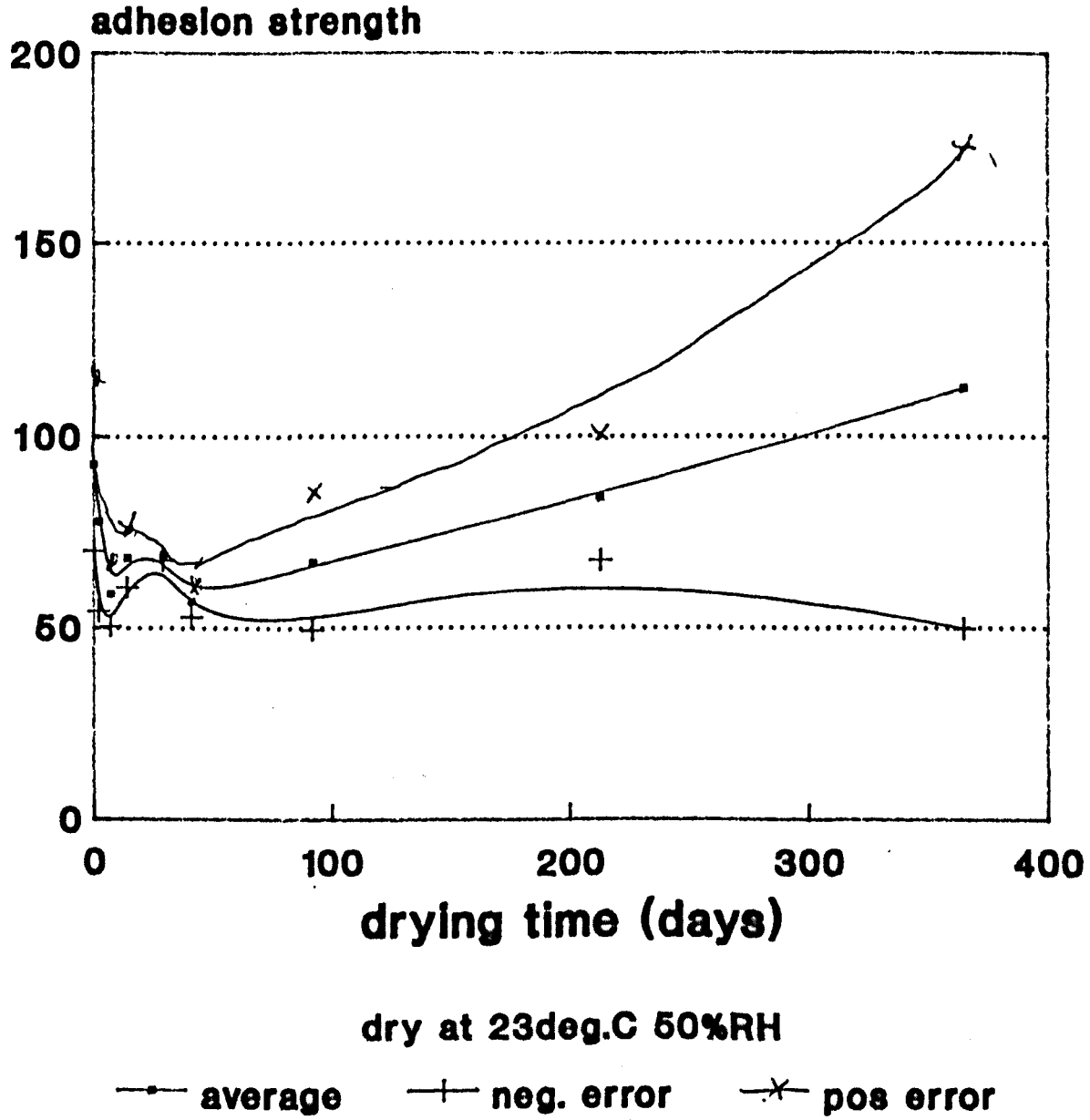
RATE OF BOUNDARY CHANGE

against adhesion loss



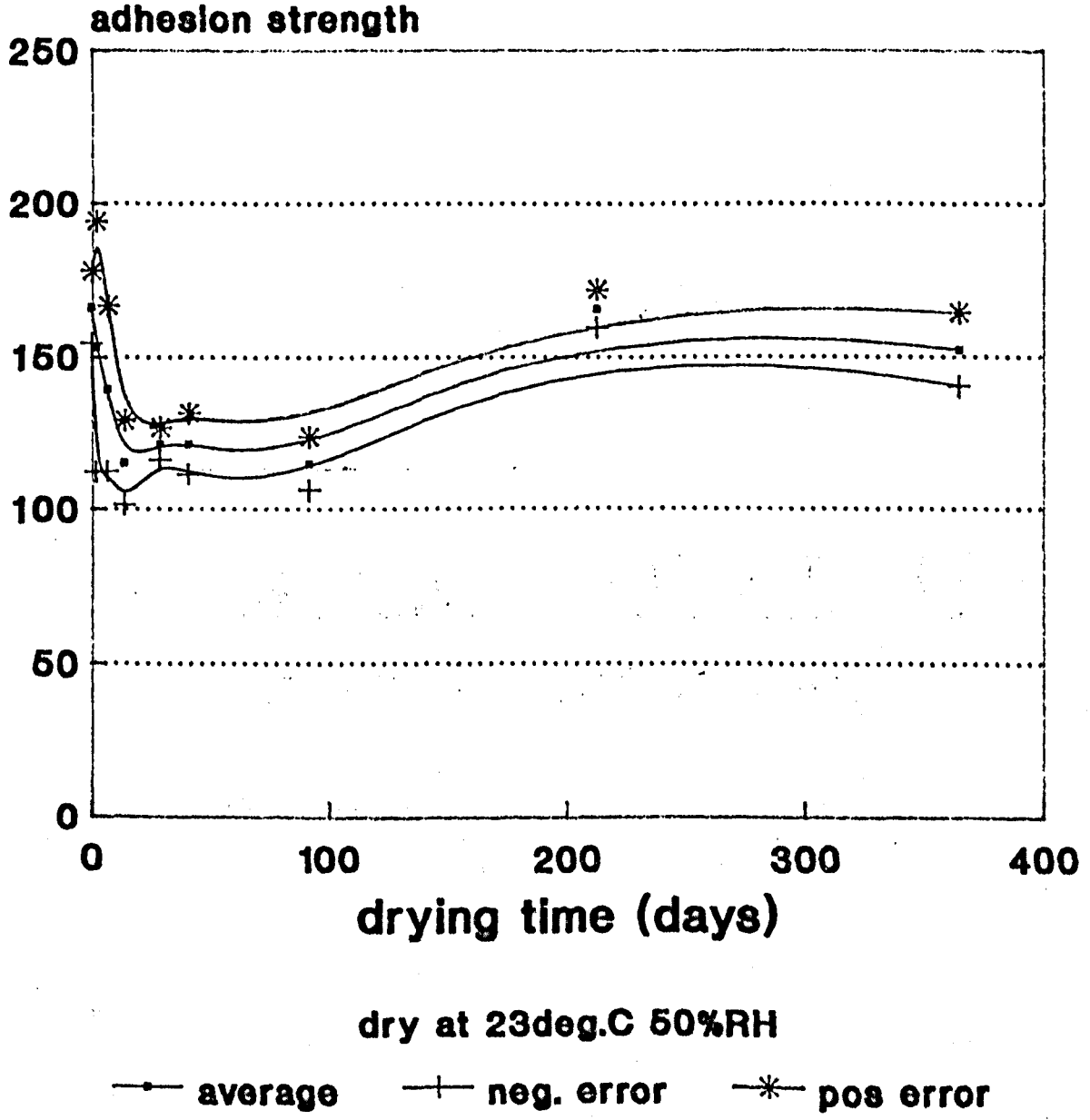
X96/2B

ADHESION BUILD-UP
after 1 year ageing



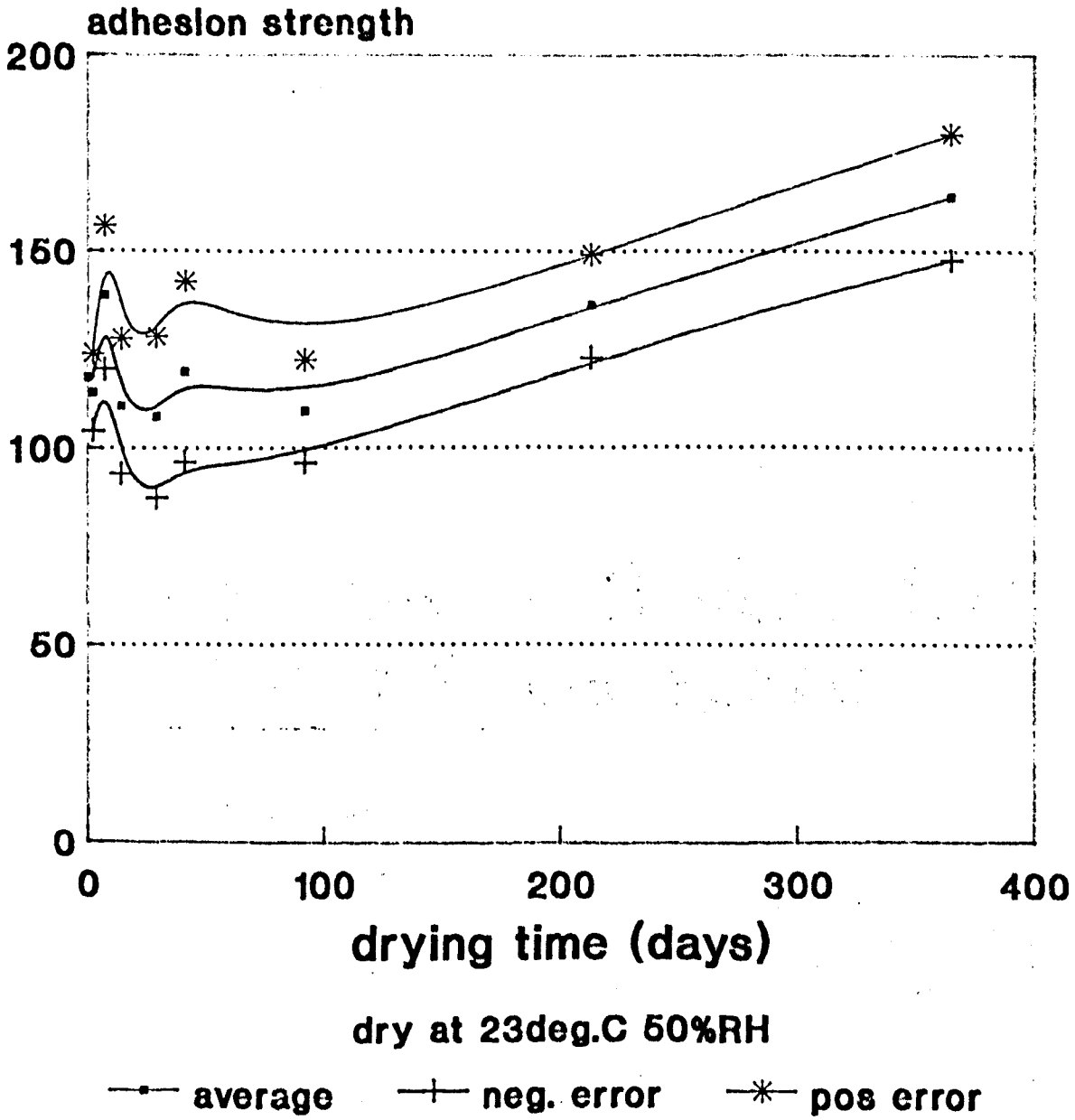
X1

ADHESION BUILD-UP
after 1 year ageing



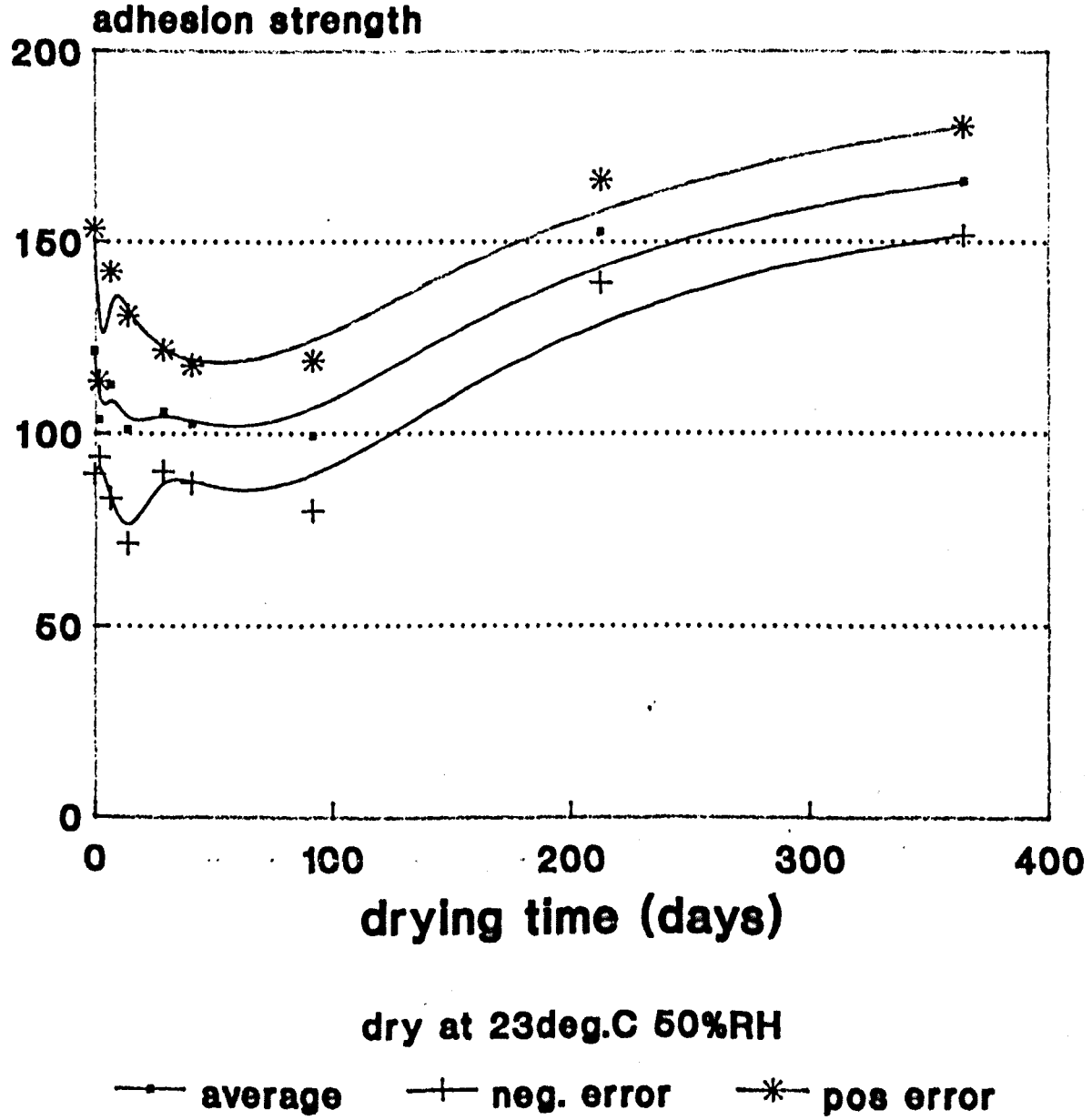
X2

ADHESION BUILD-UP
after 1 year ageing



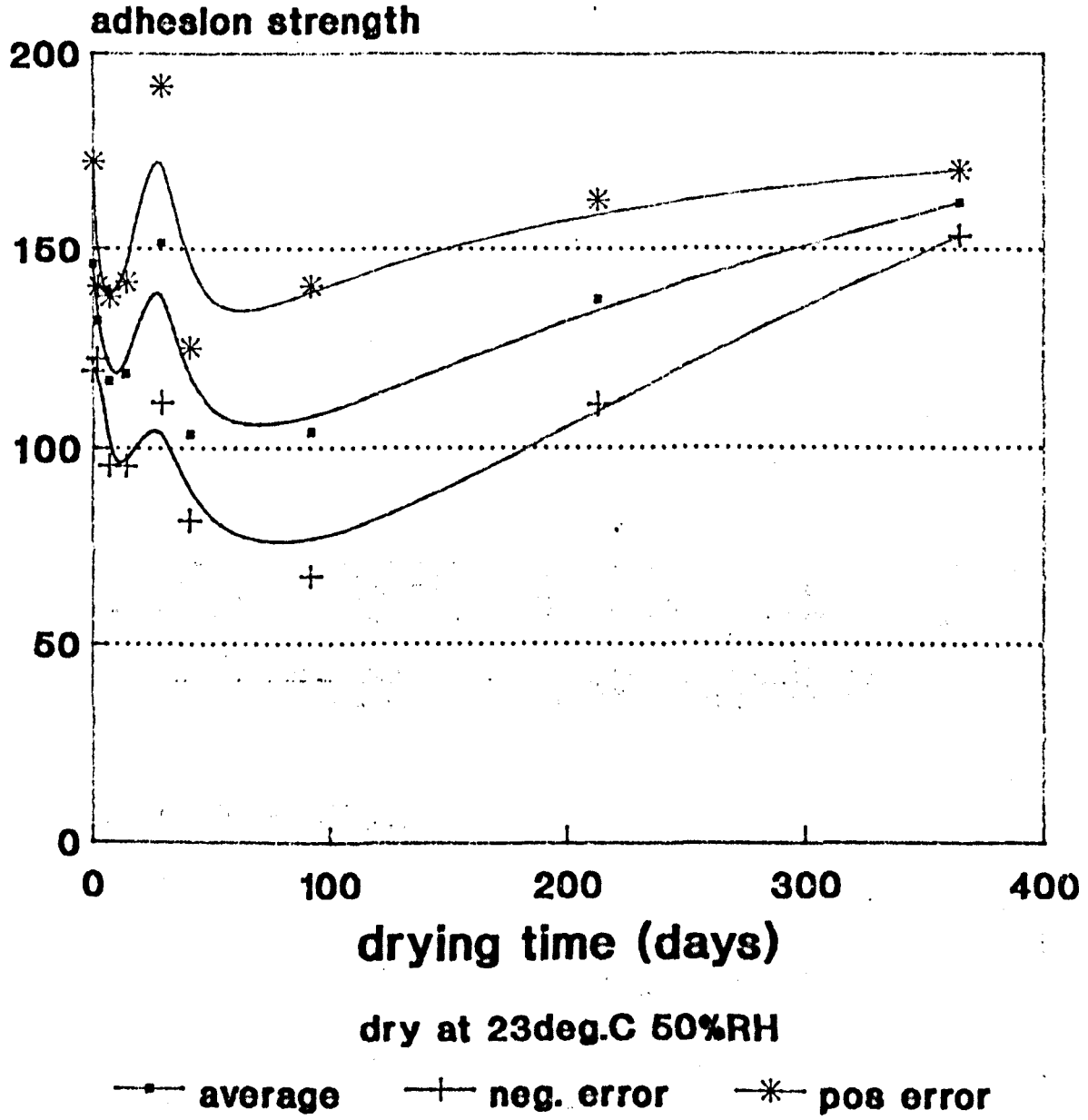
X3

ADHESION BUILD-UP
after 1 year ageing



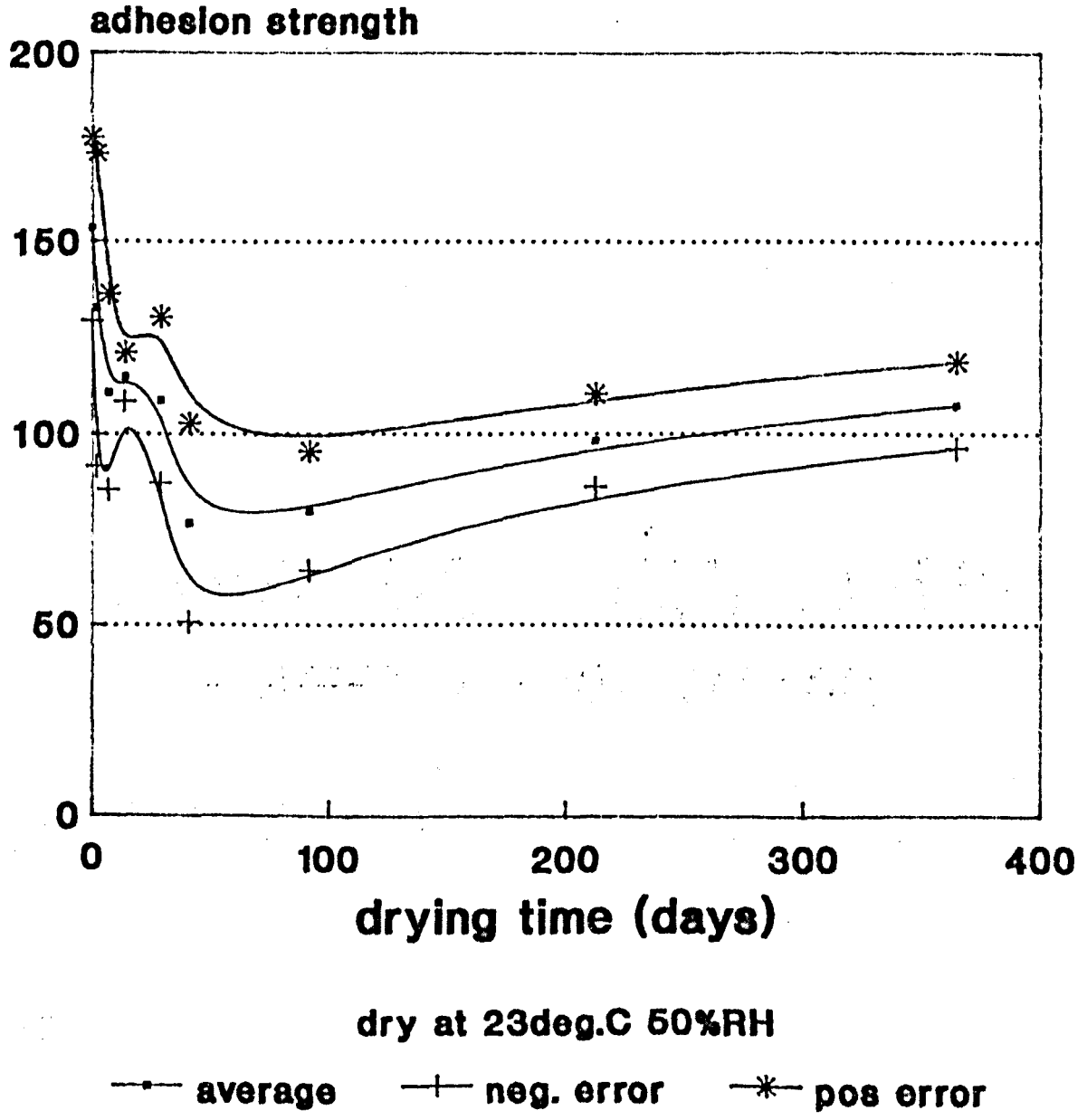
X4

ADHESION BUILD-UP
after 1 year ageing



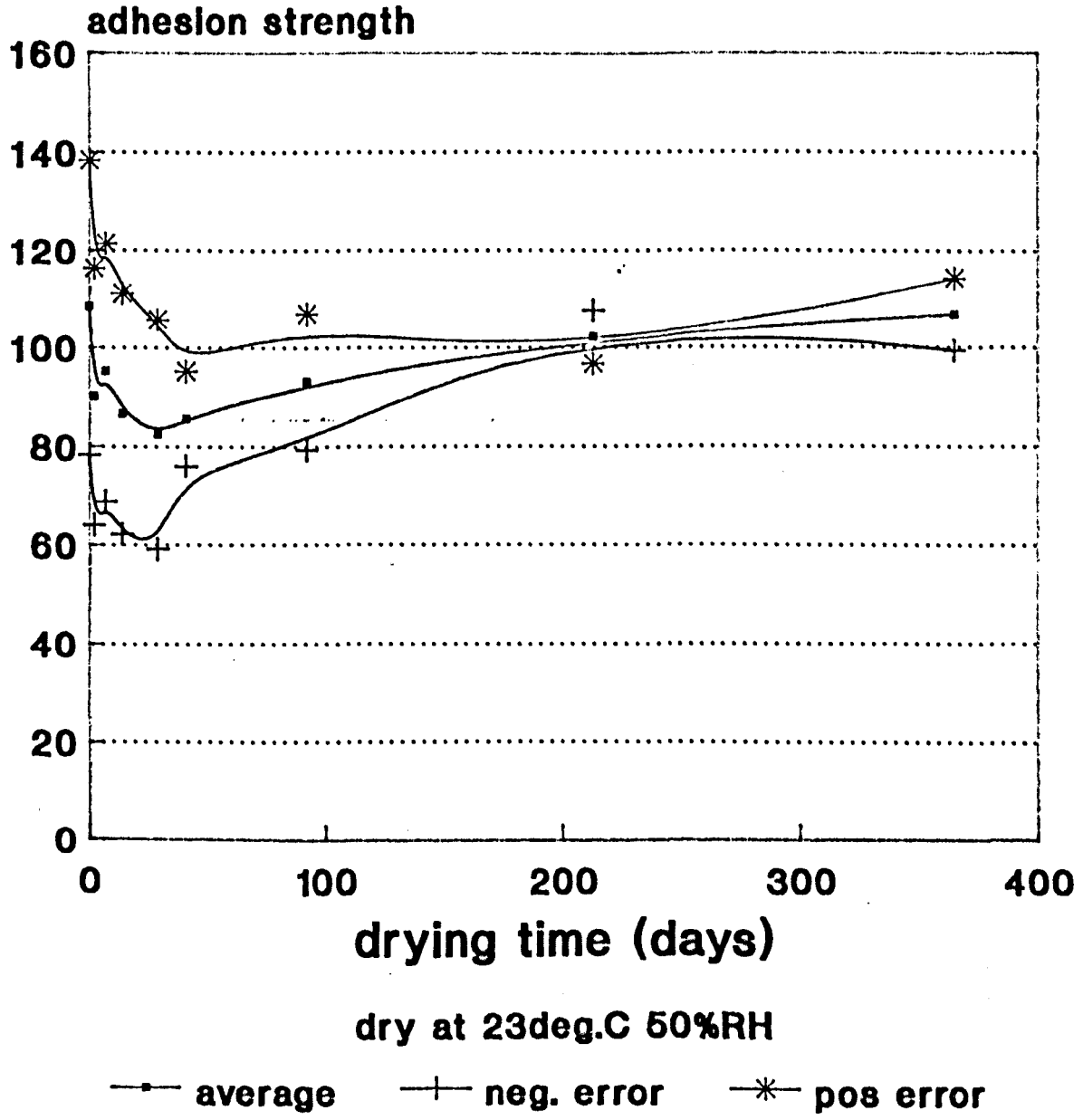
X7

ADHESION BUILD-UP
after 1 year ageing



X8

ADHESION BUILD-UP
after 1 year ageing



X9

COMPUTER PROGRAMMES

CALCULATION OF WORK OF ADHESION

```
100 REM "calculation of work of adhesion in the dry and error"
101 LPRINT "calculation of work of adhesion in the dry"
102 INPUT "enter sample number";X
LPRINT "saple ";X
110 REM "D=dispersion, P=polar, A = adhesive, S = substrate"
220 INPUT "enter dispersive component of adhesive";da
230 INPUT "enter polar componentof adhesive";pa
240 INPUT "enter dispersive component of polymer";dp
245 INPUT "enter polar component of polymer";pp
246 INPUT "error in da";dda
247 INPUT "error in pa";dpa
248 INPUT "error in dp";ddp
249 INPUT "error in pp";dpp
250 w = 2*SQR (dp*da) + 2*SQR(pp*pa)
260 PRINT "work of adhesion =";w
LPRINT "work of adhesion = ";w
265 j = dp/da*dda^2
270 k = da/dp*ddp^2
280 l = pp/pa*dpa^2
290 m = pa/pp*dpp^2
300 dw = SQR (j+k+l+m)
PRINT "error in work of adhesion =";dw
LPRINT "ERROR IN WORK OF ADHESION =";DW
320 GOTO102
```

CALCULATION OF WORK OF ADHESION IN THE PRESENCE OF WATER

```
100 REM "calculates werror of work of adhesion in the presence of water"
110 REM "D=dispersion, P=polar, A=adhesive, S=substrate"
112 LPRINT "error in presence of water"
114 INPUT "enter sample number";x
116 LPRINT "sample";x
220 INPUT "enter dispersive component of adhesive";da
230 INPUT "enter polar component of adhesive";pa
240 LET dp = 1.75
245 LET pp = 126.33
246 INPUT "error in da";dda
247 INPUT "error in pa";dpa
248 LET ddp = -5.854
249 LET dpp = 54.034
250 w = 2*SQR(dp*da) + 2*SQR(pp*pa)
260 PRINT "work of adhesion = ";w
261 LET ph = 51
262 LET dh = 21.8
265 j = dp/da*dda^2
270 k = da/dp*ddp^2
280 i = pp/pa*dpa^2
290 m = pa/pp*dpp^2
292 n = dh/da*dda^2
294 p = ph/pa*dpa^2
296 q = dh/dp*dpp^2
298 r = ph/pp*dpp^2
300 dw = SQR(j+k+l+m+n+p+q+r)
305 PRINT "error in work of adhesion =";dw
307 LPRINT "work of adhesion = ";w
LPRINT "error in work of adhesion =";dw
320 GOTO 114
```

CALCULATION OF WORK OF ADHESION
IN THE PRESENCE OF A LIQUID

```
100 REM "calculation of work of adhesion in the presence of a liquid"
103 INPUT "enter sample number";a
105 REM  "L = liquid"
110 REM "D = dispersion, P = polar, A = adhesive, S = substrate"
111 LPRINT "sample number is ";a
112 INPUT "enter dispersive component of liquid l ";dl
113 INPUT "surface tension of liquid l";st
115 pl =st-dl
220 INPUT "enter dispersive component of adhesive";da
230 INPUT "enter polar component of adhesive";pa
240 INPUT "enter dispersive component of substrate";ds
245 INPUT "enter polar component of substrate";ps
250  w  =  (dl+pl-SQR(da*dl)-SQR(pa*pl)-SQr(ds*dl)-
SQR(ps*pl)+SQR(da*ds)+SQR(pa*ps)
260 LPRINT "work of adhesion is ";w
270 GOTO 103
```

CALCULATION OF CRITICAL SURFACE TENSION

```
10 REM "calculates critical surface tension"
15 LPRINT "calculations of critical surface tension from contact angle"

20 INPUT "what is sample number" ;a
25 LPRINT "sample number";a
OPTION DEGREES
30 INPUT "what is contact angle with water" ;b
35 INPUT "what is contact angle with E.D.";c
40 INPUT "what is contact angle with D.M.S.0" ;d
41 LET g = COS(b)
42 LET h = COS(c)
43 LET k = COS(d)
45 LET x = 0.25 * (1 + g) * (1 + g) * 72.2
50 LET y = 0.25 * (1 + h) * (1 + h) * 48.3
60 LET z = 0.25 * (1 + k) * (1 + k) * 43.6
70 LPRINT "surface tensions are water";x "E.D "; y "D.M.S.0"; z
```

CALCULATIONS OF DIFFUSION

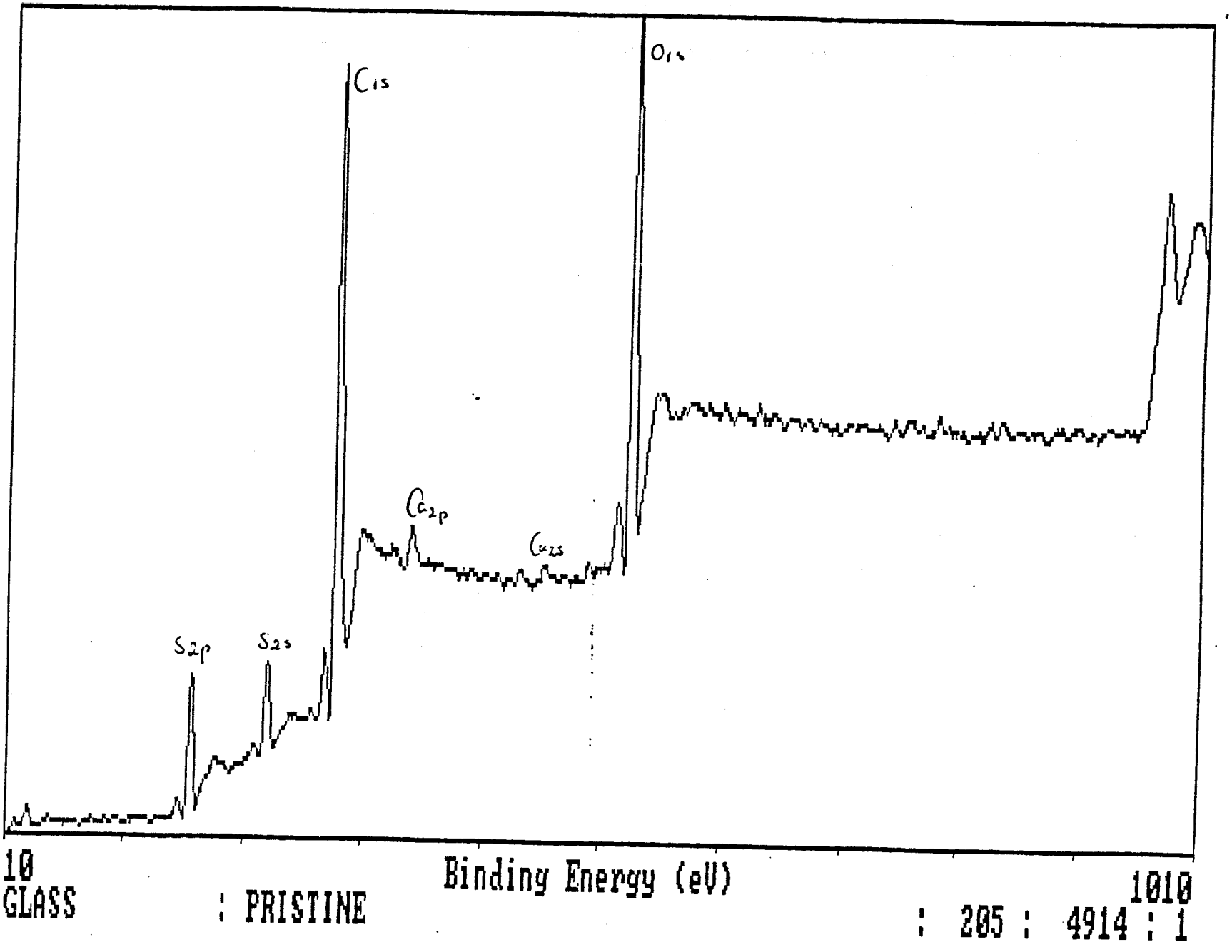
```
REM CALCULATION OF DIFFUSION
10
PRINT "what is sample reference";
INPUT a$
LPRINT "THE SAMPLE REFERENCE IS ";a$
PRINT "what is time (in days)" ;
INPUT t
LPRINT "THE TEST TIME IS ";t
PRINT "what is sample thickness";
INPUT 1
LET t=t*24*3600
PRINT "time in secs =";t

LET 1=1/1000
print "sample length in M =";1

LET d=o.049*SQR (t/l^2)
PRINT "THE DIFF. =";d
LPRINT "THE DIFFUSION COEFFICIENT IS ";d
FOR n=0 TO 5
LET b=(-d)*(2*n+1)*(2*n+1)*(3.14159^2*t)/(4*1^2)
LET x=EXP (b)
LET y=COS ((2*n+1)*(3.14159)/(2*1))
LET z=((-1^n)/(2*n+1))

LET c=(4/3.14159)*z*x*y
LET c=c+c
PRINT "N = ";n
PRINT "C = ";c

NEXT n
LPRINT "THE UNIFORM INITIAL DISTRIBUTION IS ";1-c
LPRINT "
LPRINT "
PRINT "what is M infinity";
INPUT m
PRINT "what is M initial";
INPUT o
LET s=(m\o)*100
LET p=s*d
LPRINT "THE PERMEATION FACTOR IS ";p
LPRINT "          "
LPRINT "          "

GOTO 10
```

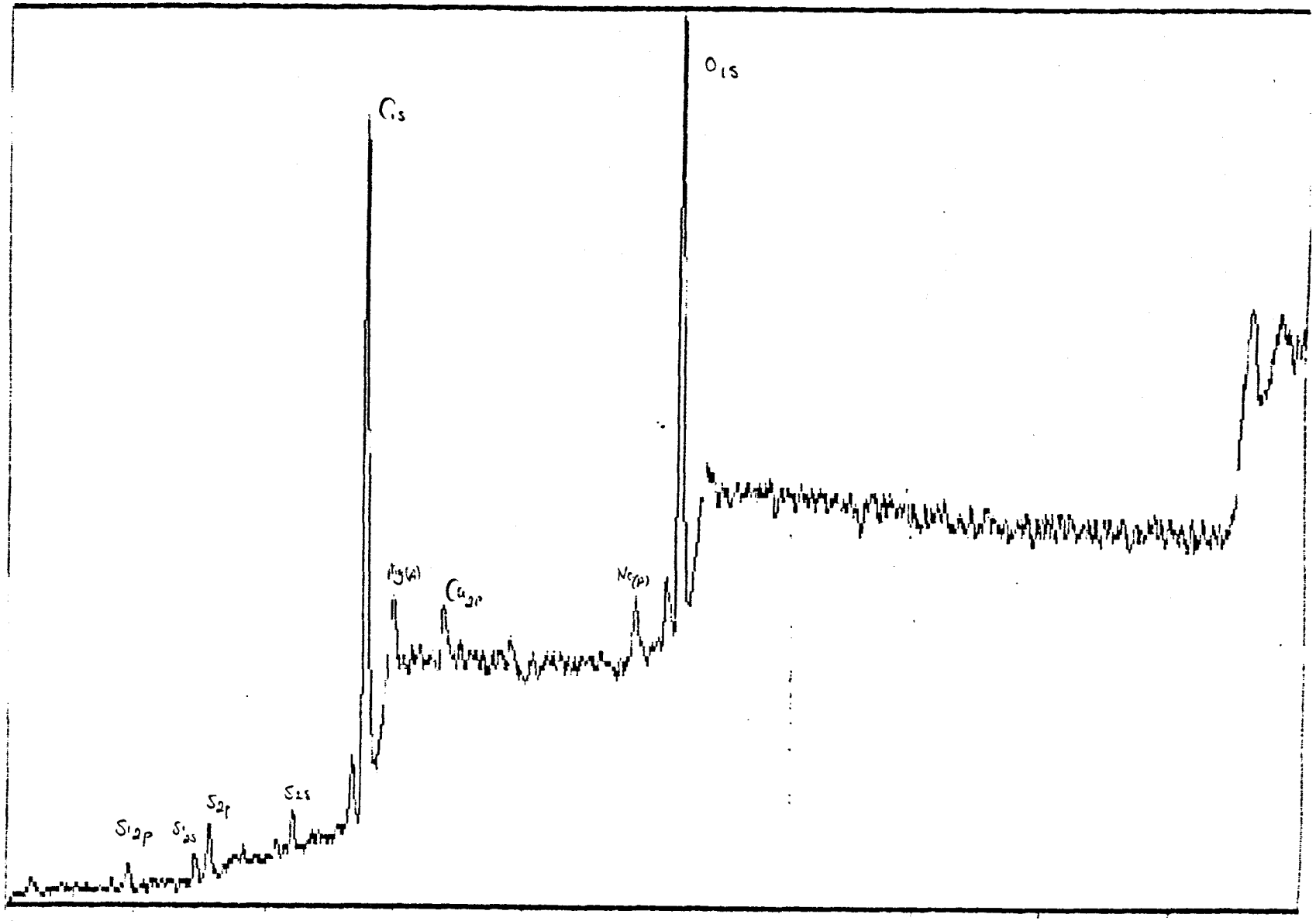
CALCULATES SURFACE ENERGY FROM CONTACT ANGLE

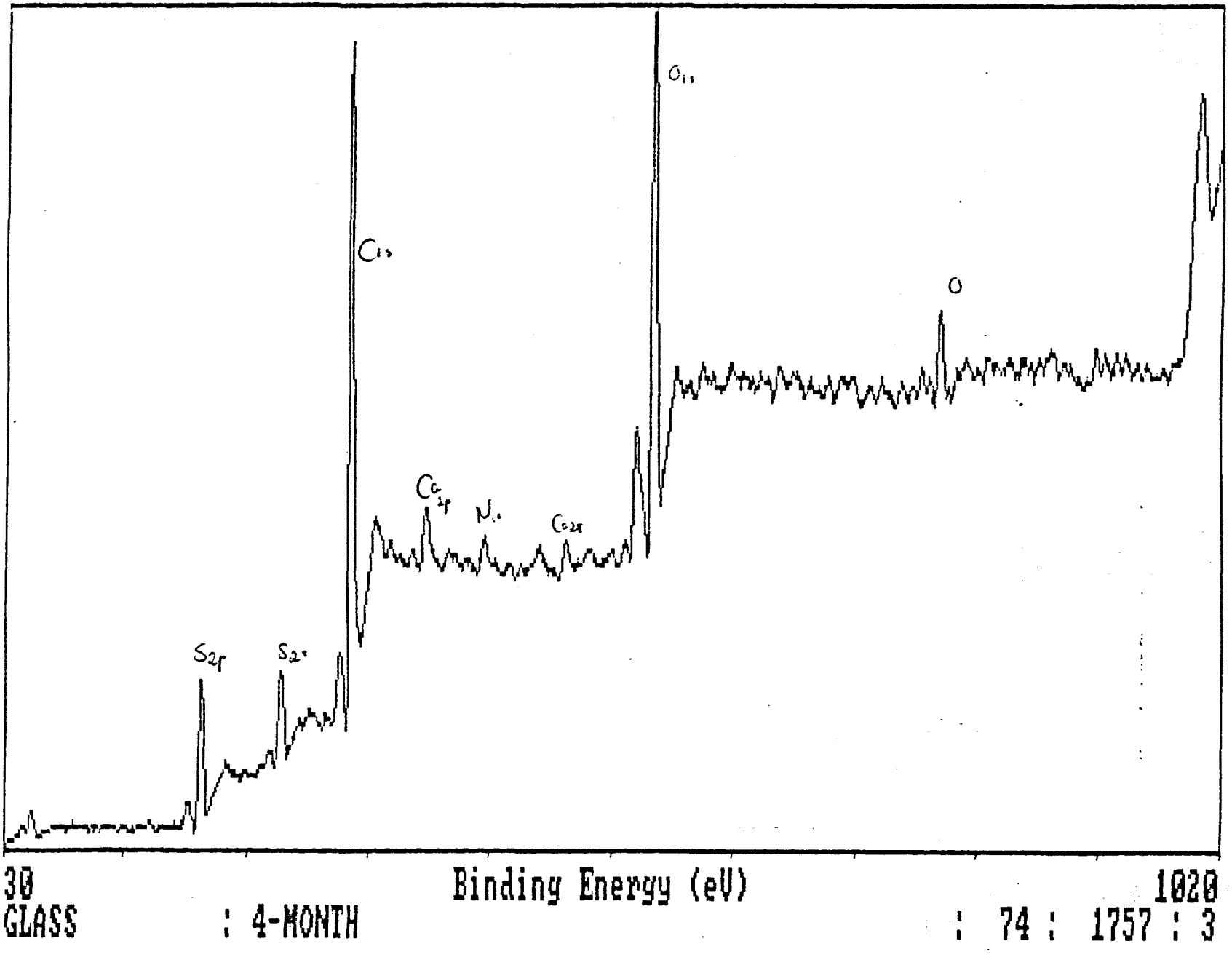
```
50 REM calculates dispersive and polar components of surface energy from
51 REM  contact angles of three liquids (water, ethanediol, and dmso)
55 LPRINT "calculated dispersive and polar components of "
56 LPRINT "surface energy from contact angle"
57 LPRINT "sample       gd          dgd          gp          dgp"

75  INPUT "sample identification";z
100 INPUT "water contact angle" ;cw
110 INPUT "ED contact angle" ;cw
120 INPUT "DMSO contact angle" ;ce
120 INPUT "DMSO contact angle" ;cs
190 a  = 0.01745
200 yw = 7.796*(1+COS(a*ce))
220 ys = 3.687*(1+COS(a*cs0)
300 xw = 1.529
310 xe = 0.805
320 xs = 0.5
410 sy = yw+ye+ys
430 sxy = xw*yw + xe*ye + xs*ys
500 b = (sy*3.386 - 3.222*sxy)/3.1627
510 r = (4*sxy - 3.222*sy)/3.1627
600 d1 = r*xy + b - yw
610 d2 = r*xe + b - ye
620 d3 = r*xs + b - ys
650 sd = d1^2 + d2^2 + d3^2
660 db = SQR (sd*0.5353)
670 dr = SQR (sd*0.63237)
700 gd = b*b
710 dgd = 2*b*db
720 gp = r*r
730 dgp = 2*r*dr
800 PRINT "dispersive component = "; gd
810 PRINT "error = "; dgd
820 PRINT "polar component = ";gp
830 PRINT "error = "; dgp
850 LPRINT "X" =      gd          dgd          gp          dgp
860 GOTO 75
```

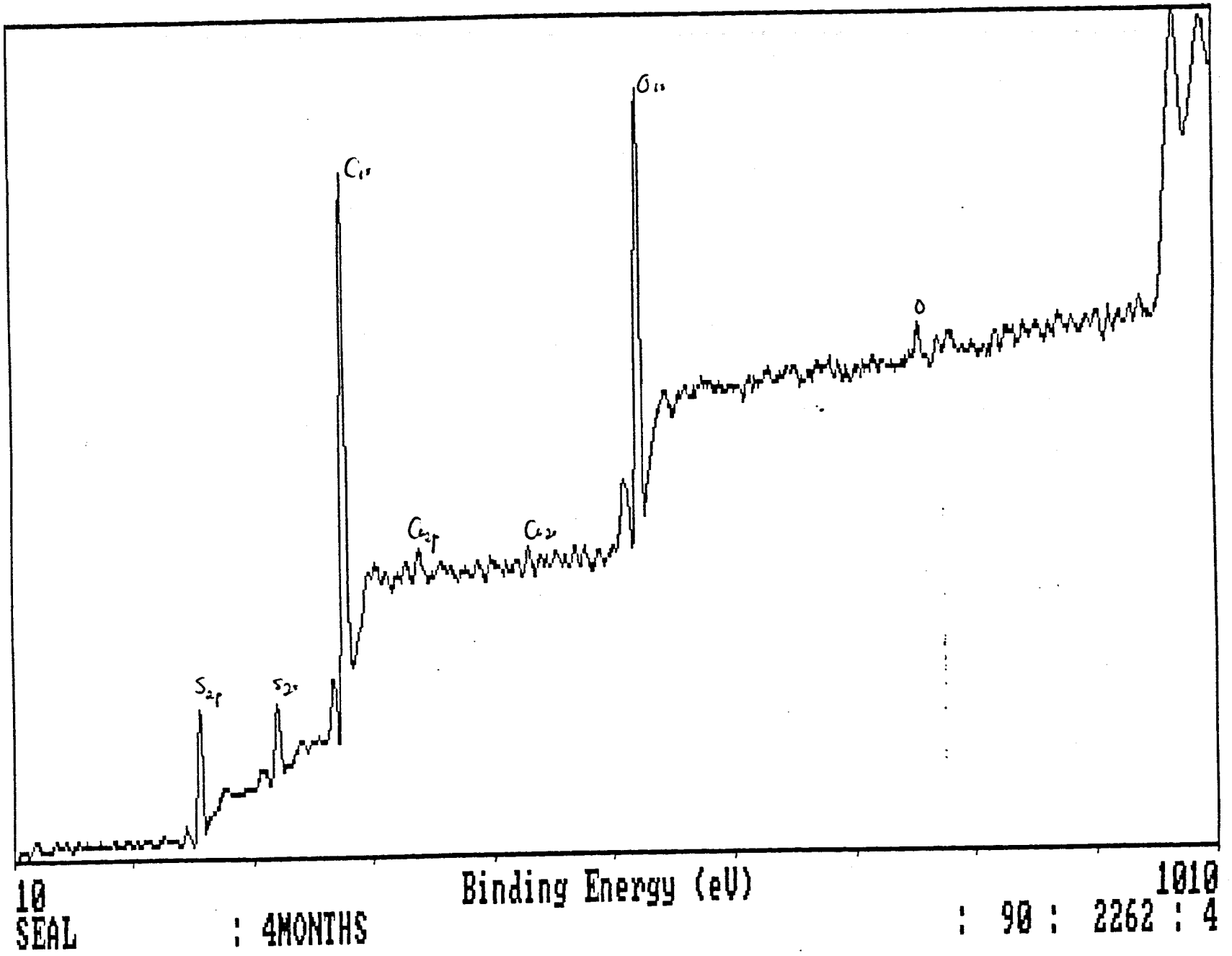
CALCULATIONS WORK OF ADHESION FROM SURFACE TENSION

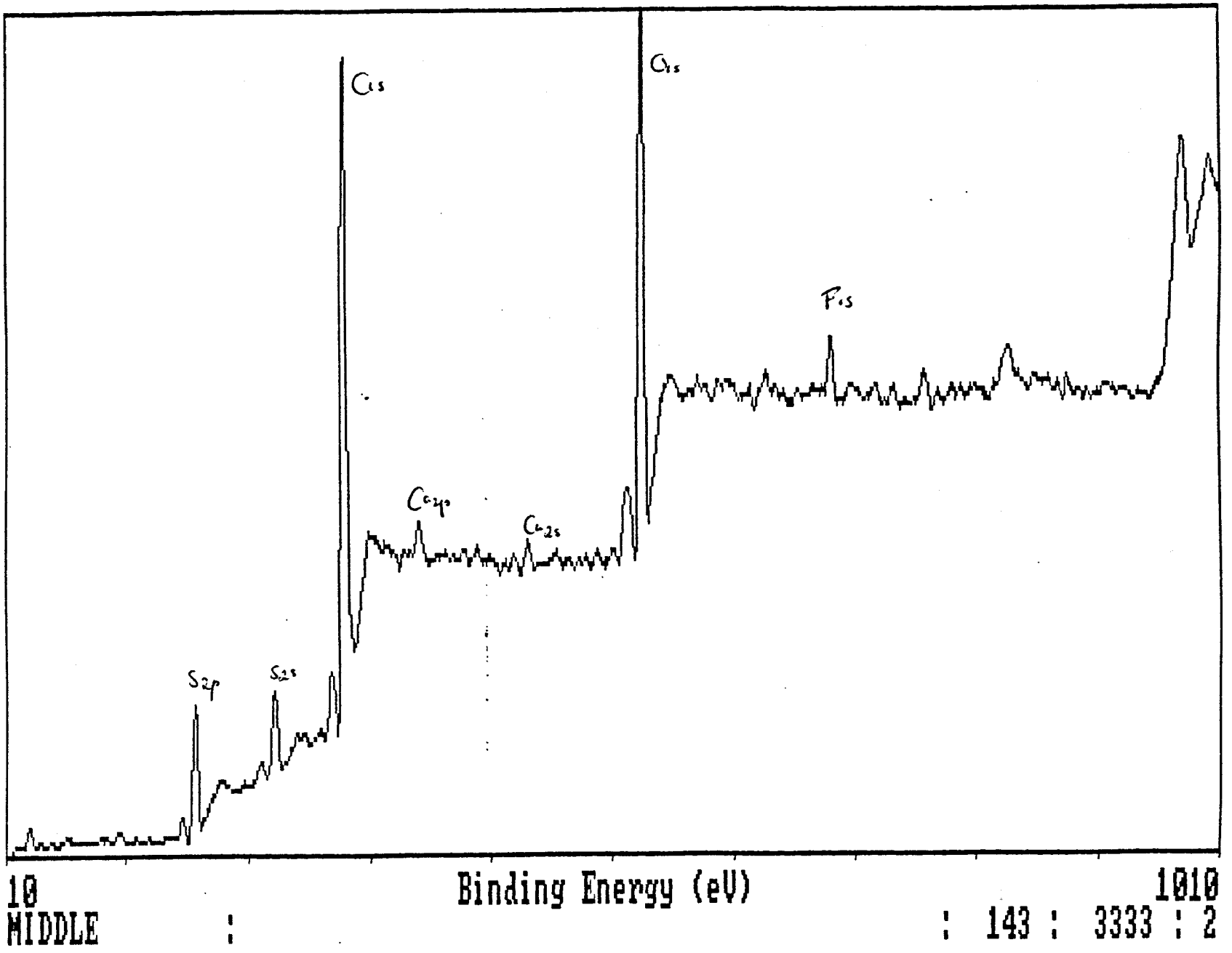
```
10 REM calculates work of adhesion from surface tension
15 LPRINT "work of adhesion of cured film from surface tension"
17 LPRINT "based on graphical interpretion"
20 INPUT "sample reference number" ; a
25 LPRINT "sample reference number is ";a
30 INPUT "dispersive component of sample";b
35 INPUT "polar component of sample";c
40 LET "d = d/b (b + c)
45 LET p = c/(b + c)
50 LET x = 16/63.26
55 LET y = 47.26/63.26
60 LET t = SQR (d*x) + SQR (p&y)
70 LET w = 2 * t * SQR ((b+c) * 63.26)
75 LPRINT "the work of adhesion of ";a " = " ;w
80 GOTO 20
```


C1s
O1s
Ca2p
Ca2s
S2p
S2s
10
Binding Energy (eV)
1010
GLASS : PRISTINE
: 205 : 4914 : 1

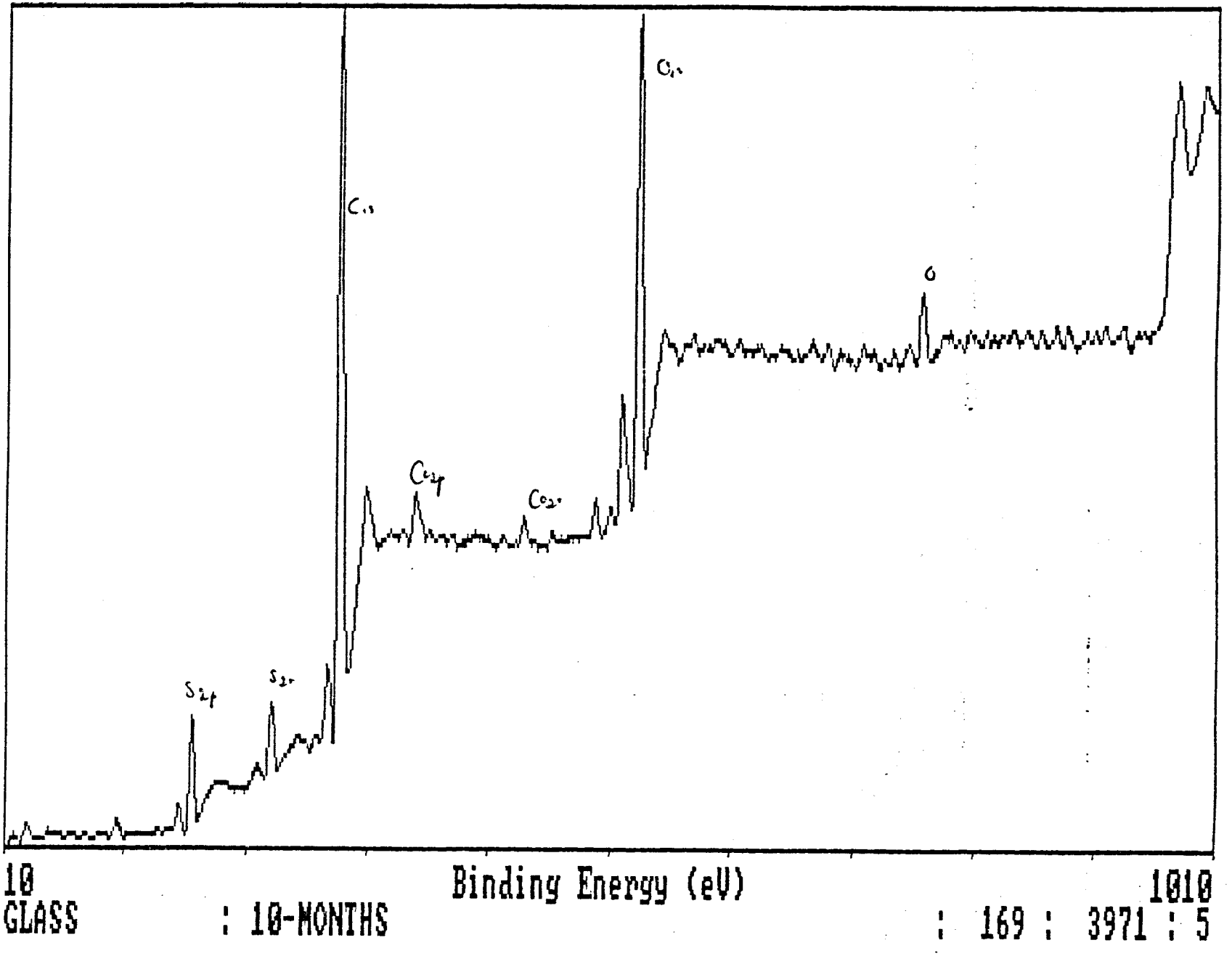

O1S
C1S
Mg(A)
Cu2P
Ne(P)
Si2P
Si2S
S2P
S2S
10
Binding Energy (eV)
1010
3MONTH
: 39 : 1710 : 1

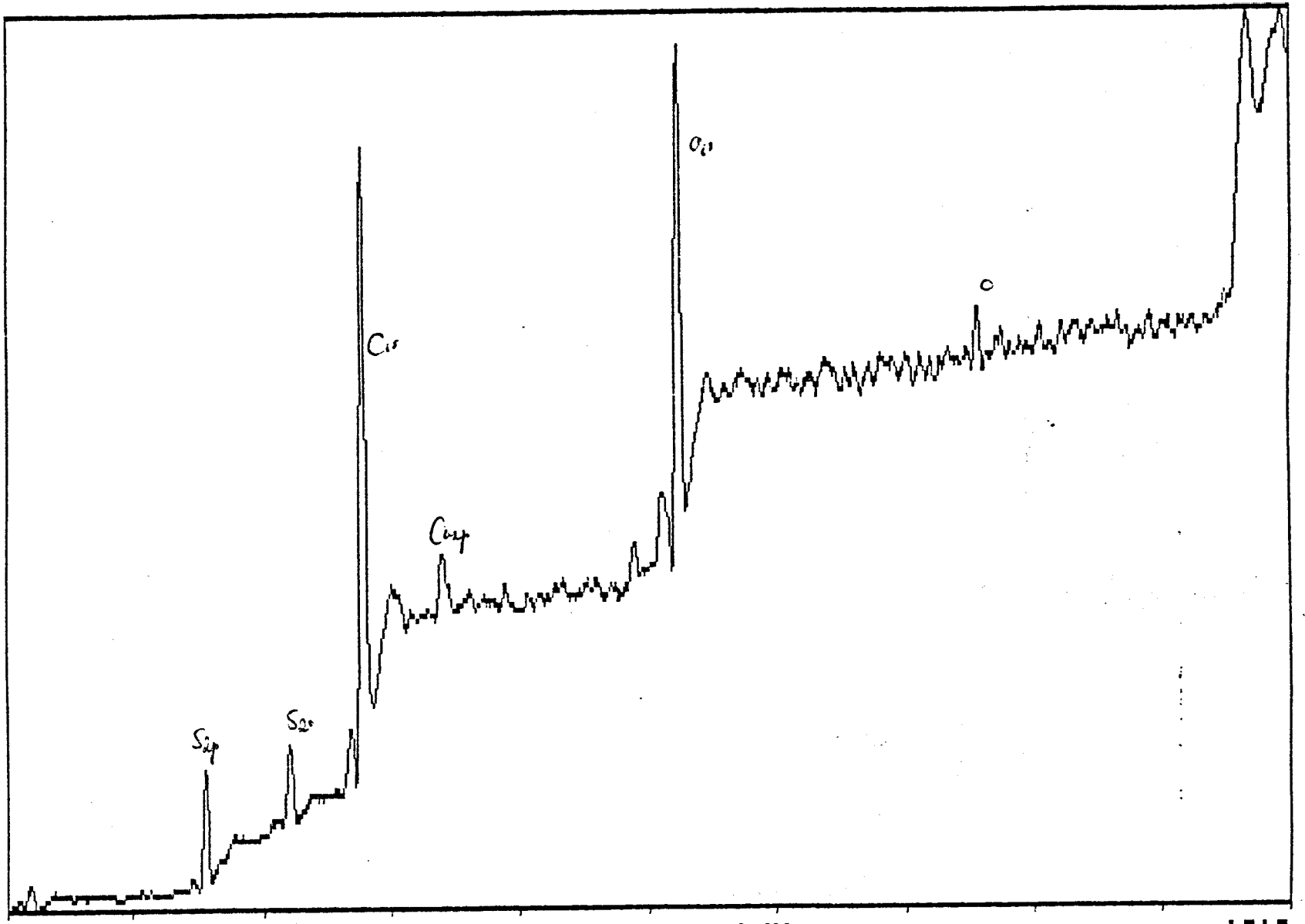

O1s
C1s
O
Co2p
N1s
Co2s
S2p
S2s
30
Binding Energy (eV)
1020
GLASS : 4-MONTH : 74 : 1757 : 3


O1s
C1s
C2p
C2s
S2p
S2s
O
10
Binding Energy (eV)
1010
SEAL : 4MONTHS
: 90 : 2262 : 4


C1s
O1s
F1s
Co2p
Co2s
S2p
S2s
10
Binding Energy (eV)
1010
MIDDLE
: 143 : 3333 : 2

10
Binding Energy (eV)
1010
10MONTHGLASS :
: 36 : 1389 : 2


Cl2p
Cl2s
C1s
Ca2p
Ca2s
O
S2p
S2s
10
Binding Energy (eV)
1010
GLASS : 10-MONTHS : 169 : 3971 : 5



10 Binding Energy (eV) 1010

SEAL : 10-MONTHS : 108 : 2399 : 6